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# A NEW EFFECT OF HYDROGEN BOND FORMATION (CHELATION)

## Part IV. Abnormal Behaviour of 2′-Hydroxy Flavanones

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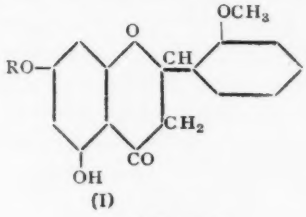
Anthoxanthins with a substituent in the 2′-position are rare in nature and citronetin has been considered to be the only representative of this type among flavanones. It was found to be present in the peels of *Citrus limon ponderosa* as its glycoside citronin (I*a*) by Yamamoto and Oshima[1] who gave it the constitution of 5:7-dihydroxy-2′-methoxy flavanone (I*b*). By the fusion of the glycoside with potash they claimed to have isolated the phloroglucinol part containing the sugar residue and *o*-methoxy-hydrocoumaric acid. Later Shinoda and Sato[2] reported the synthesis of a compound of this constitution from phloroglucinol and *o*-methoxy cinnamoyl chloride by the Friedel and Craft's reaction. But there is no agreement between the natural and synthetic products and their derivatives. Citronetin obtained from citronin was given a melting point of 204° while the compound obtained by synthesis had a melting point of 224–25°. Their methyl ethers also did not agree in their melting points. Further it has been noticed by us that the Friedel and Crafts reaction with *o*-methoxy cinnamoyl chloride and phloroglucinol does not proceed smoothly and that good results are obtained only with the trimethyl ether of phloroglucinol.



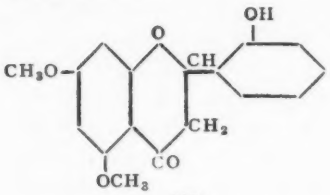

(I)

*a*, R = Sugar
*b*, R = H

In view of these discrepancies it was planned to investigate the preparation of 2′-hydroxy flavanones and their conversion to the corresponding flavones and flavonols. In the course of this work

were noticed certain extraordinary features which had not been observed before and some of these are discussed in this communication.

The following ketones were condensed with salicylaldehyde in the presence of cold aqueous alcoholic potash: (i) phloracetophenone dimethyl ether, (ii) γ-resacetophenone monomethyl ether, (iii) gallacetophenone 3:4-dimethyl ether, and (iv) resacetophenone 4-methyl ether. The initial yellow colour of the solutions very rapidly changed to deep red and on acidification after 48 hours the products were almost colourless and crystalline in all the cases except in the last one where a semi-solid mass was obtained. With all the products a bright red colour was developed when their alcoholic solutions were treated with magnesium and hydrochloric acid and the Boric-Citric reaction[3] was negative. These reactions indicated that they consisted of flavanones and they were free from chalkones. The products seemed to be quite pure and their structures should be correctly represented by formulæ II to V. In a test case phloracetophenone-4:6-dimethyl ether and salicylaldehyde were condensed by the acid method of Russel and Todd.[4] Besides a deeply coloured product (probably a pyrylium salt) a colourless crystalline compound was obtained in the more soluble fraction and it was found to be identical with the product obtained by the alkali method.



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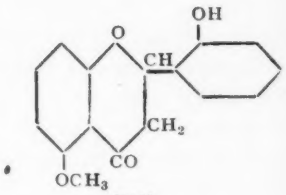

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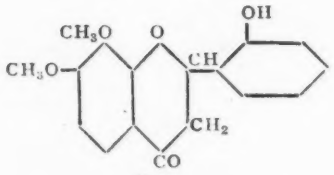

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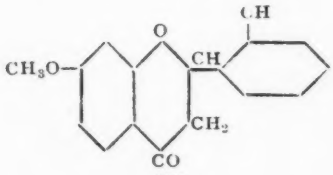
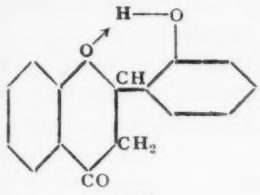


(V)

An extraordinary characteristic of the above-mentioned 2′-hydroxy flavanones is the prominent ferric chloride colour in alcoholic solution. They are also sparingly soluble in aqueous alkali and highly resistant to methylation. These properties are reminiscent of 5-hydroxy flavanones[5] and should be attributed to the existence of chelation involving the 2′-hydroxyl and the oxygen atom of the pyranone ring as shown in formula VI. Since the

chelate ring consists of six atoms it could be expected to be stable but no earlier observation has been recorded regarding the existence of chelate rings of this type and of their stability. That ether oxygen can act as donor in hydrogen bond formation is fairly well recognised and the existence of this phenomenon was brought out prominently in the study of hydrogen bonds by the Raman effect by Murty and Seshadri.[6]

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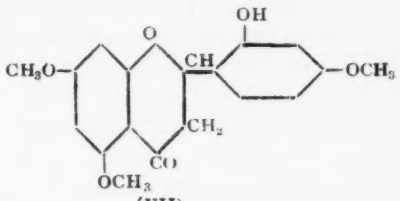
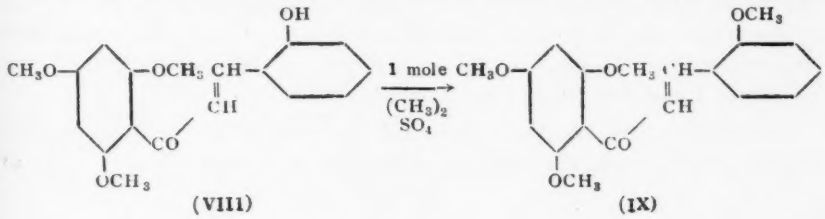



(VII)

As a further extension of this study the condensation of phloracetophenone dimethyl ether with the 4-methyl ether of resorcylaldehyde was also carried out. The behaviour of the product was exactly the same and its constitution should be that of the 2′-hydroxy flavanone (VII). The exclusive formation of 2′-hydroxy flavanones under conditions of chalkone condensation seems to be attributable to the existence of the above-mentioned chelation which renders the flavanone structure highly stable. In this respect also the 2′-hydroxyl group resembles in its effect the 5-hydroxyl, which has been shown to stabilise the flavanone ring in the earlier papers of this series.[5]

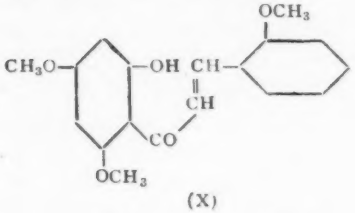
From the experiments discussed above it would appear that the products are flavanones because free hydroxyl groups were present in the 2-and 2′-positions of the intermediate chalkones, the former rendering the closure of the flavanone ring possible and the latter stabilising it. In order to verify this conclusion two sets of experiments were conducted. In the first, a fully methylated ketone, phloracetophenone trimethyl ether was condensed with salicylaldehyde. The product was a chalkone (VIII) giving no colour with magnesium and hydrochloric acid but responding to the Boric-Citric reaction. This substance was already reported by Cullinane and Philpott[7] and can be fully methylated to the tetramethoxy chalkone (IX), identical



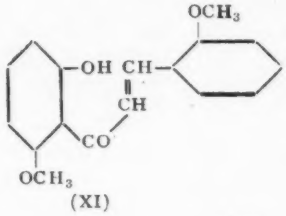

(VIII) (IX)

with the sample prepared by the chalkone condensation between phloracetophenone trimethyl ether and salicylaldehyde methyl ether and by the condensation of phloroglucinol trimethyl ether and *o*-methoxy cinnamoyl chloride in cold ether solution by means of aluminium chloride.

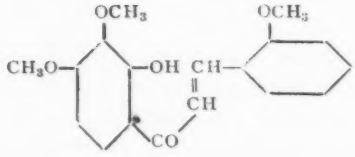
The second set of experiments employed the methyl ether of salicylaldehyde and the first three *o*-hydroxy acetophenones mentioned earlier. In many of the condensations 2-hydroxy chalkones (X to XII) were obtained. It was at the same time observed that in certain condensations the products were mainly the corresponding 2′-hydroxy flavanones which after a few crystallisations were found to be identical with the samples obtained earlier using salicyaldehyde for the condensation. Similar results were obtained using phloracetophenone dimethyl ether and resorcylaldehyde dimethyl ether. In one of the condensations a pure 2-hydroxy chalkone[8] (XIII) was produced while in some others a mixture consisting mostly of the 2′-hydroxy flavanone was produced.



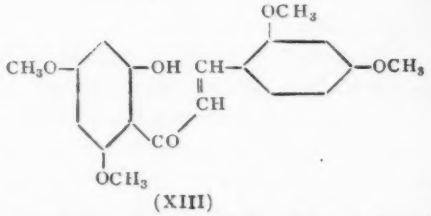
(X)



(XI)



(XII)



(XIII)

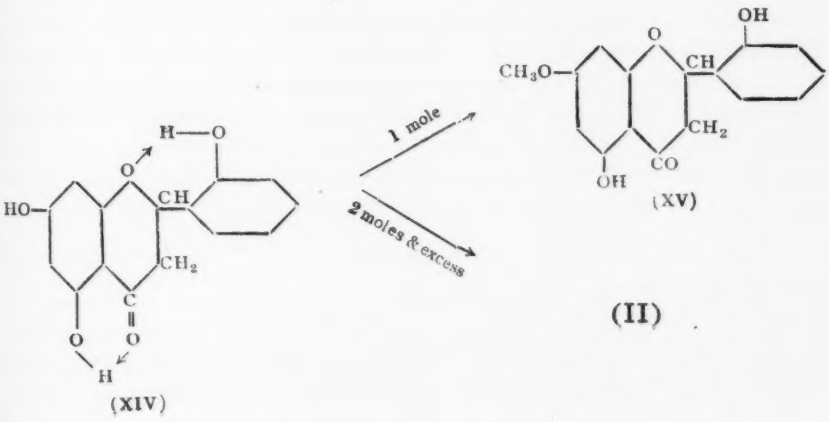
The demethylation of the 2′-methoxyl group in alkaline medium in the cold is quite unusual and it would appear that the initial flavanone ring closure which has been reported to take place in other cases of chalkones[9] even in alkaline medium renders the demethylation of 2′-methoxyl easy. The highly alkaline conditions used in these condensations seem also to play an important part for when a mild alkali like sodium ethoxide is employed this demethylation does not take place to any appreciable extent and 2-hydroxy chalkones are invariably obtained.

Another interesting observation was made when the above-mentioned 2-hydroxy chalkones were refluxed with alcoholic sulphuric acid (4%) to

bring about flavanone ring closure. With ring closure simultaneous demethylation of the 2′-position also takes place yielding in quantity the corresponding 2′-hydroxy flavanone. This further confirms the conclusion already arrived at that a methoxyl in the 2′-position of a flavanone is highly susceptible to demethylation.

For the demethylation of flavanones hydriodic acid has not been found to be successful since some unknown changes occur. On the other hand the use of anhydrous aluminium chloride for this purpose has been found to be quite convenient.[10] The hydroxy flavanones thus obtained are colourless and crystalline in appearance. The most unexpected observations of this work were made in the experiments on the methylation of hydroxy flavanones mentioned above. Complete methylation of these does not occur even under the most efficient conditions using dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium. In previous studies on the methylation of hydroxy flavanones it was shown that of all the hydroxyls the 7-hydroxyl is the most reactive and partial monomethyl ethers could be satisfactorily obtained.[11] Further methylation without opening the pyranone ring is possible so long as the 5-hydroxyl group is free. As soon as this is also methylated the oxygen ring opens up and eventually fully methylated chalkones result.[5]

In the course of the present work the first case to be examined was 5:7:2′-trihydroxy flavanone (XIV); with one mole of dimethyl sulphate it yields the 7-monomethyl ether (XV) and with 2 moles 5:7-dimethoxy-2′-hydroxy flavanone (II) with the pyranone ring still in tact and the product identical with that obtained by direct condensation of phloraceto-




(II)

phenone dimethyl ether and salicylaldehyde. Prolonged heating with large excess of dimethyl sulphate did not bring about further methylation.

7 : 8 : 2′-Trihydroxy flavanone yielded only 7 : 8-dimethyl ether with excess dimethyl sulphate and 5 : 2′-dihydroxy flavanone gave only the 5-methyl ether. Thus the 2′-hydroxyl group is not only more resistant to methylation than the 5-hydroxyl but it cannot be methylated at all by methods now employed. This is a very remarkable result and the special features of the concerned chelate structure (VI) which would account for this phenomenon are not at present comprehensible.

In the light of the special features connected with 2′-hydroxy flavanones and the related chalkones certain difficulties reported in earlier literature become explicable. In the course of their synthesis of morin, Kostanecki, Lampe and Tambor[11] prepared 2-hydroxy-4 : 6 : 2′ :4′-tetramethoxy chalkone; when they converted it into the corresponding flavanone by the usual method they obtained only poor yields. Further they had difficulty in converting it into the flavonol, the conversion being accompanied by partial demethylation. They concluded that the resulting morin trimethyl ether had a free hydroxyl group in the 5-position due to this partial demethylation. But such a demethylation of the 5-methoxyl group during the flavonol conversion was not noticed in other similar cases (*eg.*, kaempferol methyl ether by Kostanecki *et al.*[13]). In view of our observations that the same 2-hydroxy-4 : 6 : 2′ : 4′-tetramethoxy chalkone undergoes demethylation at the 2′-position during isomerisation to the flavanone, complications should be expected in the progress of their synthesis.

More recently Cullinane and Philpott[7] experienced difficulty in preparing 2-hydroxy-4 : 6 : 2′ : 4′-tetramethoxy chalkone; their product melted at 128° while our sample had a melting point of 152–53° agreeing with the description of Kostanecki *et al.*[8] The lower melting point is obviously due to contamination with the corresponding 2′-hydroxy flavanone formed in the condensation. Their conditions involving some heating would have favoured the demethylation of the 2′-position. As already mentioned the most satisfactory method for obtaining these methoxy chalkones seems to be the use of sodium ethoxide as the condensing agent.

## EXPERIMENTAL

5 : 7-*Dimethoxy*-2′-*hydroxy flavanone* (*II*)

(i) To a solution of phloracetophenone dimethyl ether (2·5 g.) and salicylaldehyde (1·4 c.c.) in alcohol (30 c.c.) was added potassium hydroxide (10 g. in 10 c.c. of water) with shaking. It was kept in an air-tight flask

or two days, when the solution turned deep red. It was then diluted with water and acidified after cooling with hydrochloric acid. The pale yellow solid that separated was filtered, washed with a saturated solution of sodium bicarbonate and finally with water. It crystallised from alcohol as aggregates of colourless plates melting at 85–86°. Yield 2 g. It gave a deep blue colour with concentrated nitric acid, a violet colour with ferric chloride and a red colour with magnesium and hydrochloric acid. It was sparingly soluble in aqueous sodium hydroxide (Found: C, 61·9; H, 6·2; $C_{17}H_{16}O_5$, 1·5 $H_2O$ requires C, 62·4; H, 5·8%). Even after sublimation at reduced pressure on a water bath the compound had the same melting point and did not lose its water of crystallisation.

(ii) Through a solution of phloracetophenone dimethyl ether (2 g.) and salicylaldehyde (0·8 c.c.) in ethyl acetate cooled in ice, dry hydrogen chloride gas was passed for three hours when a deep brown coloured solid was formed. After leaving for 24 hours in the ice-chest the solid was filtered and was found to be amorphous (m.p. above 300°); this was not examined further. On distilling off ethyl acetate from the filtrate a pale yellow solid separated which crystallised from alcohol as colourless plates melting at 85–86°, identical with the product of experiment (i).

5:7:2′-*Trihydroxy flavanone* (*XIV*)

To a solution of 5:7-dimethoxy-2′-hydroxy flavanone (1 g.) in benzene (50 c.c.) anhydrous aluminium chloride (4 g.) was added and the mixture refluxed on a water bath for 2 hours. Benzene was then removed by distillation and the complex decomposed with ice and hydrochloric acid when a white solid separated out. The mixture was kept in a hot water bath for a few minutes to complete the decomposition. On cooling a colourless solid separated which crystallised from alcohol in the form of colourless rectangular prisms melting at 195–96° (Shinoda and Sato gave m.p. 185–87° for nor-citronetin). It dissolved readily in aqueous sodium carbonate and gave a pink colour with ferric chloride. It could be recovered unchanged from its alkaline solution on acidification (Found: C, 61·7; H, 4·9, loss on drying 6·8%; $C_{15}H_{12}O_5$, $H_2O$ requires C, 62·1; H, 4·8, loss on drying 6·2%).

*Methylation*

(*a*) *With one mole of dimethyl sulphate* (*7-methoxy-5:2′-dihydroxy flavanone*) (*XV*).—A solution of 5:7:2′-trihydroxy flavanone (1·6 g.) in dry acetone (100 c.c.) was refluxed with dimethyl sulphate (0·6 c.c.) and anhydrous potassium carbonate (2 g.) for 6 hours. It was then filtered,

the residue washed with warm acetone and acetone distilled off. 7-Methoxy-5: 2′-dihydroxy flavanone crystallised from alcohol in the form of colourless aggregates of rhombohedral prisms melting at 134–35°. It gave a deep violet colour with ferric chloride and a blue colour with concentrated nitric acid (Found: C, 67·1; H, 5·3; $C_{16}H_{14}O_5$ requires C, 67·2; H, 4·9%).

(*b*) *With two moles of dimethyl sulphate* (5: 7-*dimethoxy*-2′-*hydroxy flavanone*) (*II*).—5: 7: 2′-Trihydroxy flavanone (0·3 g.) was methylated with dimethyl sulphate (0·26 c.c., 2 moles) and anhydrous potassium carbonate (1 g.) in acetone solution for 16 hours. The product crystallised from alcohol in the form of aggregates of plates melting at 85–86°. It agreed in all its properties and reactions with 5: 7-dimethoxy-2′-hydroxy flavanone and a mixed melting point with the sample obtained earlier was undepressed.

(*c*) *With excess dimethyl sulphate*.—The trihydroxy flavanone was refluxed with dimethyl sulphate (excess) and potassium carbonate for 48 hours. On working up as usual the product was found to be the dimethoxy-monohydroxy-flavanone (II).

2-*Hydroxy*-4: 6: 2′-*trimethoxy chalkone* (*X*)

This was reported earlier by Bargellini and Peratoner.[14] In two experiments phloracetophenone dimethyl ether and salicylaldehyde methyl ether in alkaline medium gave mostly the 5: 7-dimethoxy-2′-hydroxy flavanone at room temperature. However by carrying out the reaction at 0° and working up as usual 2-hydroxy-4: 6: 2′-trimethoxy chalkone was obtained which cyrstallised from alcohol as bright yellow rectangular plates and needles melting at 113–14° (Bargellini and Peratoner reported m.p. 106–08°). It gave only a brown colour with nitric acid and a reddish brown colour with ferric chloride. On reduction with magnesium and hydrochloric acid it did not develop any red colour (Found: C, 68·6; H, 5·7; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%).

*Isomerisation with alcoholic sulphuric acid*

The above chalkone (0·5 g.) was refluxed in alcoholic sulphuric acid solution (50 c.c., 4%) for 24 hours. On concentrating under reduced pressure and diluting the solution with water a colourless crystalline solid was obtained. It was filtered, washed with water and crystallised from alcohol when it separated in the form of colourless rectangular plates melting at 85–86°. The product could easily be sublimed under reduced pressure on a water bath when it was obtained as thick plates, m.p. 85–86°. It was identical in all its properties with 5: 7-dimethoxy-2′-hydroxy flavanone

(II) and a mixed melting point with the sample obtained in an earlier experiment was undepressed.

2:4:6:2′-*Tetramethoxy chalkone* (*IX*)

*Method I.*—Phloracetophenone trimethyl ether (2 g.) and salicylaldehyde methyl ether (2 c.c.) in alcohol (50 c.c.) were treated with a solution of potassium hydroxide (6 g. in 6 c.c.) and the solution left corked for two days. On diluting with water and cooling a pale yellow solid separated which was filtered and washed with water. It crystallised from alcohol as stout rectangular prisms melting at 124–25°. It was insoluble in aqueous alkali and gave no colour with ferric chloride (Found: C, 69·1; H, 6·3; $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

*Method II.*—Anhydrous aluminium chloride (10 g.) was dissolved in dry ether with cooling and phloroglucinol trimethyl ether added to it. The mixture was cooled in ice and treated with *o*-methoxy cinnamoyl chloride (4 g.) with shaking. It was kept at 0° for half an hour and at the room temperature for 12 hours. Ether was then distilled off and the complex decomposed with ice and hydrochloric acid. The product was filtered, washed with dilute hydrochloric acid and water. It crystallised from alcohol as big pale yellow rectangular prisms melting at 124–25°. It was identical with the sample obtained in Method I.

*Method III.*—2:4:6-Trimethoxy-2′-hydroxy chalkone (0·5 g.) was methylated with excess of dimethyl sulphate and potassium carbonate in acetone solution. The tetramethoxy chalkone crystallised from alcohol as stout prisms melting at 124–25° and was identical with the samples obtained above.

5:7:4′-*Trimethoxy-2′-hydroxy flavanone* (*VII*)

(i) Phloracetophenone dimethyl ether (3 g.) and resorcylaldehyde-4-methyl ether (2·7 g.) were condensed in alkaline medium as described earlier for similar cases. The product obtained on acidification crystallised from alcohol as colourless plates melting at 86–87° and after sublimation melted at the same temperature. It gave a blue colour with conc. nitric acid, a violet colour with ferric chloride and a red colour with magnesium and hydrochloric acid. Thus it agreed in its properties with those required for a flavanone (Found: C, 62·4; H, 5·6; $C_{18}H_{18}O_6$, $H_2O$ requires C, 62·1; H, 5·8%).

(ii) 5:7:2′:4′-Tetrahydroxy flavanone described below was methylated with excess of dimethyl sulphate and potassium carbonate in acetone solution for 20 hours. The product crystallised from alcohol as rectangular

plates and prisms melting at 86–87° and was identical with the product of the above experiment (i).

5 : 7 : 2′ : 4′-*Tetrahydroxy flavanone*

A solution of 5 : 7 : 4′-trimethoxy-2′-hydroxy flavanone (0·5 g.) in benzene (10 c.c.) was treated with anhydrous aluminium chloride (2·5 g.) and the product worked up as in similar demethylation given before. The product crystallised from alcohol as colourless prisms melting at 184–86°. It gave a pink colour with ferric chloride in alcoholic solution and dissolved readily in aqueous sodium carbonate (Found: C, 55·5; H, 4·8; $C_{15}H_{12}O_6$, 2 $H_2O$ requires C, 55·5; H, 4·9%).

2-*Hydroxy*-4 : 6 : 2′ : 4′-*tetramethoxy chalkone* (*XIII*)

Kostanecki and Tambor[8] employed aqueous sodium hydroxide for the condensation. In our experiment the same general procedure as was used in the case of salicylaldehyde methyl ether was adopted. It was found that in one of the condensations the product was found to be pure chalkone and was obtained in good yield. It crystallised from alcohol as yellow stout rhombohedral prisms melting at 152–53°. It gave no colour with concentrated nitric acid and magnesium and hydrochloric acid. In alcoholic solution it gave a brown colour with ferric chloride.

However it was found that in a number of condensations the product was mostly the 2′-hydroxy flavanone (VII) agreeing with the earlier sample. Even under exactly the same conditions as adopted by Kostanecki and Tambor the same demethylation of the 2′-position was noticed. It should be noted in this connection that Cullinane and Philpott[7] report a melting point of 128° for this chalkone; their sample was probably a mixture.

*Isomerisation with alcoholic sulphuric acid*

The pure chalkone obtained above was refluxed with alcoholic sulphuric acid (50 c.c., 4%) for 24 hours and the solution concentrated under reduced pressure. The solid that separated on dilution was filtered and crystallised from alcohol. It separated as colourless thin plates melting at 84–85°. It was identical in all its properties and reactions with 5 : 7 : 4′-trimethoxy-2′-hydroxy flavanone and a mixed melting point with the sample described earlier was undepressed.

5-*Methoxy*-2′-*hydroxy flavanone* (*III*)

(i) 5-Methoxy-2′-hydroxy flavanone obtained by condensing 2-hydroxy-6-methoxy acetophenone and salicylaldehyde in alkali crystallised from alcohol in the form of colourless long rectangular prisms melting at 55–56°,

It gave a green colour with nitric acid and a red colour with magnesium and hydrochloric acid (Found: C, 66·4; H, 6·0; $C_{16}H_{14}O_4$, $H_2O$ requires C, 66·7; H, 5·6%).

(ii) 5: 2′-Dihydroxy flavanone described below was methylated with dimethyl sulphate (1·1 mole) and anhydrous potassium carbonate in acetone solution (16 hours). The methyl ether crystallised from alcohol as colourless long rectangular prisms melting at 55–56°, was identical with the product of experiment (i) and the mixed melting point with it was not depressed.

5: 2′-*Dihydroxy flavanone*

On demethylating the above compound with aluminium chloride as in previous cases 5: 2′-dihydroxy flavanone was obtained which crystallised from alcohol as rectangular prisms melting at 153–54°. It gave a deep reddish violet colour with ferric chloride and dissolved in aqueous sodium hydroxide (Found: C, 70·2; H, 5·0; $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7%).

2-*Hydroxy*-6: 2′-*dimethoxy chalkone* (*XI*)

When aqueous sodium hydroxide was used for the chalkone condensation the reaction was accompanied by the usual demethylation of the 2′-position resulting in the formation of 2′-hydroxy flavanone. However by adopting the following method the pure chalkone could be obtained.

Sodium (3 g.) was dissolved in absolute alcohol (20 c.c.) and to this was added a solution of 2-hydroxy-6-methoxy acetophenone (1·4 g.) and salicylaldehyde methyl ether in alcohol. After leaving the mixture in the refrigerator for 2 days it was diluted with water, extracted with ether and the aqueous solution acidified with hydrochloric acid. A semi-solid mass was obtained which solidified on keeping in ice. It was filtered, washed with aqueous sodium bicarbonate and finally with water. On crystallising from alcohol it was obtained as bright orange red stout rhombic prisms melting at 96–97°. It gave a reddish brown colour with ferric chloride, no colour with conc. nitric acid and no red colour with magnesium and hydrochloric acid (Found: C, 71·8; H, 5·5; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%).

7: 8-*Dimethoxy*-2′-*hydroxy flavanone* (*IV*)

(i) This was obtained from gallacetophenone dimethyl ether and salicylaldehyde. The product crystallised from alcohol as colourless stout rectangular prisms melting at 79–80°, gave a violet colour with ferric chloride and a red colour with magnesium and hydrochloric acid (Found: C, 60·7; H, 6·0; $C_{17}H_{16}O_5$, $2\,H_2O$ requires C, 60·7; H, 5·9%).

(ii) Methylation of 7: 8: 2′-trihydroxy flavanone with excess of dimethyl sulphate gave only the 2′-hydroxy flavanone identical in all its reactions with the above sample.

7: 8: 2′-*Trihydroxy flavanone*

This was obtained by demethylation of 7: 8-dimethoxy-2′-hydroxy flavanone with anhydrous aluminium chloride. It separated from alcohol as colourless aggregates of needles melting at 165–66°. It gave a bluish violet colour with ferric chloride and dissolved readily in aqueous sodium carbonate (Found: C, 58·5; H, 5·3; $C_{15}H_{12}O_5$, 2 $H_2O$ requires C, 58·4; H, 5·2%).

2-*Hydroxy*-3: 4: 2′-*trimethoxy chalkone* (*XII*)

Gallacetophenone dimethyl ether (2 g.) and salicylaldehyde methyl ether (2 g.) were condensed in alcoholic solution in the presence of potassium hydroxide (6 g.). On working up as in similar cases the product crystallised from alcohol as bright yellow prisms melting at 103–04°. It gave a reddish brown colour with ferric chloride and no colour with magnesium and hydrochloric acid (Found: C, 68·4; H, 5·9; $C_{18}H_{18}O_5$ requires C, 68·8; H, 5·7%).

7: 2′-*Dihydroxy flavanone*

7-Methoxy-2′-hydroxy flavanone obtained from peonol and salicylaldehyde separated only as a semi-solid mass and could not be crystallised. It was directly demethylated with aluminium chloride in benzene solution. The dihydroxy flavanone crystallised from alcohol as prismatic needles melting at 132–33°, and it gave a deep red colour with ferric chloride (Found: C, 62·0; H, 5·5; $C_{15}H_{12}O_4$, 2 $H_2O$ requires C, 61·7; H, 5·5%).

## SUMMARY

In view of the discrepancies in the properties of the natural and synthetic citronetin, a detailed study of 2′-hydroxy flavanones and related compounds has been made. The condensation of a number of 2-hydroxy acetophenones with salicylaldehyde and 4-methoxy salicylaldehyde yields exclusively flavanones. Protection of both the ortho hydroxyl groups of the ketone as well as the aldehyde gives the corresponding methylated chalkones. Chalkones are again formed even if a 2-methoxy ketone is condensed with an ortho hydroxy aldehyde. On the other hand, when the hydroxyl of the ketone is kept free and only the ortho hydroxyl group of the aldehyde is etherified, the product is found to be a chalkone or flavanone, depending on the conditions. Lower temperature and milder alkali avoid demethylation of

the 2′-methoxyl group and tend to produce 2′-methoxy chalkones, otherwise a flavanone is formed with the 2′-hydroxyl group free. Even during chalkone-flavanone conversion with alcoholic sulphuric acid demethylation of the 2′-methoxyl group takes place. It is clear that a free 2′-hydroxyl group stabilises the flavanone structure such as a similar group in the 5 position; and a methoxyl group in this position in a flavanone is very readily demethylated. This could be attributed to the presence of chelation between this hydroxyl and the ether oxygen of the pyranone ring. Demethylation of these flavanones can be conveniently effected using aluminium chloride to yield the hydroxy flavanones. By employing different quantities of dimethyl sulphate partial methyl ethers of the hydroxy flavanones have been obtained. A special feature is the extraordinary resistance of the 2′-hydroxyl group in a flavanone, which cannot be methylated at all under drastic conditions. These observations explain the difficulties experienced by certain workers in the preparation and utilisation of these types of compounds.

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# PHOTOCHEMICAL AFTER-EFFECT IN $H_2O_2$-$K_4Fe(CN)_6$ REACTION

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## Introduction

In a previous communication[1] (1939) the results of preliminary investigation on the decomposition of hydrogen peroxide by potassium ferrocyanide and the photochemical after-effect in this reaction were reported, and it was suggested that the after-effect of illumination in this reaction is due to the photo-formation of potassium aquopentacyanoferrite from potassium ferrocyanide.

The above reaction has been studied by a large number of workers. Kistiakowsky[2] (1900) discovered this photochemical after-effect, and studied in detail the kinetics of hydrogen peroxide decomposition and attributed the after-effect to the formation of a catalyser (possibly of a colloidal nature) from ferrocyanide under the influence of light. The decomposition of hydrogen peroxide in the presence of ferrocyanide was found to be unimolecular both before and after irradiation. Weigert[3] (1907) however, came to the conclusion that the insolation of ferrocyanide produces reaction nuclei which catalyse the decomposition of hydrogen peroxide in the dark. Amann[4] (1911) attributed the enhanced reactivity in this reaction after insolation to the production of a photo-phase, but did not describe kinetic measurements of the photochemical after-effect. Winther[5] (1920) explained this after-effect by assuming a gradual formation of an extremely stable substance from ferrocyanide and the acceleration of the decomposition of hydrogen peroxide in the dark due to its catalytic action. In view of these conflicting views regarding the origin and nature of this photochemical after-effect, a detailed kinetic investigation was carried out. As a result of this investigation, it has been possible to substantiate the suggestion originally put forward by the author that the photo-formation of potassium aquopentacyanoferrite from potassium ferrocyanide during insolation is responsible for this marked photochemical after-effect.

## Materials and Technique

A summary of the important conclusions of this investigation has already been published[6] (1947). The technique adopted in this investigation has been discussed in detail in an earlier paper by the author[1] (1939). The

experiments described here were conducted at 40° C. in the dark. The decomposition of hydrogen peroxide was followed by titration with standard potassium permanganate. The total volume of the reaction mixture was 50 c.c. in all cases. The respective concentrations of potassium ferrocyanide and hydrogen peroxide were M/320 and N/6. A standard solution of potassium permanganate (N/24·6) was used for determining the change in peroxide concentration. The amount of permanganate used up by potassium ferrocyanide has been subtracted from the total volume used in each case. It may be remarked that the gasometric method has also been used by some workers for the study of the decomposition of hydrogen peroxide[7] (Rao and Srikantan, 1933), but this method of following the decomposition of the peroxide is not reliable[8] (Bailey), and hence the titrimetric method described above was adopted in the present investigation.

The peroxide used in most experiments was prepared in the laboratory from Merck's sodium peroxide and sulphuric acid. Experiments were also performed with Merck's 12 volume peroxide. It was observed that from a phenomenal standpoint, the behaviour of the two preparations of peroxide was very similar, but relatively high values of the velocity constants were obtained with pure hydrogen peroxide prepared in the laboratory. Merck's peroxide was distinctly acidic and this fact may account for the lower rate of decomposition in this case[8] (Bailey). In other respects the inhibitors in the peroxide, acidic or otherwise, seem to exert no detectable influence on the photochemical after-effect. It is well known that hydrogen peroxide undergoes spontaneous decomposition due to the surface of the reaction vessel. Rice and Kilpatrick[9] (1927) have shown that this spontaneous decomposition is brought about by dust and motes derived from the surface of the reaction vessel, and even freshly fused glass surface gives out motes and causes heterogeneous decomposition of hydrogen peroxide. The effect of hydrogen and hydroxyl ions on the stability of hydrogen peroxide has long been recognised[11, 10, 12, 13, 14] but the exact mechanism of decomposition of hydrogen peroxide is not yet clearly understood. It was found by experiment that pyrex glass bulbs, duly cleaned and steamed before use, gave fairly reproducible results, and blank tests showed that the spontaneous decomposition of the peroxide due to the surface of the reaction vessel was inappreciable within the time limits of the experiments. The rate of this decomposition was negligible compared with the rates of the dark reaction between hydrogen peroxide and potassium ferrocyanide, and the photochemical after-effect.

Kahlbaum's analytical potassium ferrocyanide was employed in these experiments. The crystals of ferrocyanide were pale yellow and free from

brown and amber colour. Tests for potassium aquopentacyanoferrite in M/320 solution in the dark with nitrosobenzene[15] and *para*-nitrosodimethylaniline[16] were found to be negative. In connection with some experiments under nitrogen (in which oxygen was rigorously excluded) Kahlbaum's analytical potassium ferrocyanide was recrystallised from water at room temperature (18° C.), and reprecipitated with alcohol from its aqueous solution, dried and stored in the dark. The purified ferrocyanide was employed to study the action of light under nitrogen in the absence of air. This sample was found to possess the same photo-sensitivity, and the same pale yellow colour as the original Kahlbaum reagent, and its dilute solutions in the dark gave negative tests both with nitrosobenzene and *para*-nitrosodimethylaniline, thereby demonstrating the absence of detectable amounts of complex aquosalt.

Conductivity water was used for the preparation of all solutions. Freshly prepared solutions were used in these experiments unless otherwise stated. The pyrex glass bulbs used as reaction vessels were cleaned with hot solution of chromic acid, thoroughly washed and well steamed and dried before use.

## Dark Reaction between Hydrogen Peroxide and Potassium Ferrocyanide

Freshly prepared hydrogen peroxide and ferrocyanide solutions were mixed in the dark in measured quantities, and the rate of decomposition was followed by taking out 5 c.c. of the reaction mixture at suitable intervals and determining the change in peroxide concentration by titration with standard permanganate. Kistiakowsky[2] (1900) has found this decomposition to be unimolecular, and the following figures also show that the decomposition of hydrogen peroxide by potassium ferrocyanide follows the unimolecular law. The unimolecular velocity constants calculated by the usual equation, $K = 1/t \log a/a - x$, are fairly constant. In this formula, '$t$' represents time in minutes, '$a$' the initial concentration of peroxide in terms of the volume (c.c.) of permanganate, and '$x$' the change in peroxide concentration in time '$t$'.

While studying the dark reaction, it was accidentally found that aged solutions of potassium ferrocyanide under otherwise identical conditions are slightly less reactive than fresh solutions in the initial stage of the reaction. This point was followed up by studying the dark reaction, using ferrocyanide solution which had stood in the dark for about a week. The results obtained are shown in Table II. The dark reaction was next studied by using a solution of ferrocyanide which had been heated to about 90° C. for ten

TABLE I

*With freshly prepared solution*

| $t$ | $a-x$ | K. $10^6$ |
|---|---|---|
| 0 | 20·50 | .. |
| 55 | 19·70 | 315 |
| 121 | 18·60 | 350 |
| 227 | 17·05 | 353 |
| 368 | 14·80 | 385 |

TABLE II

*With one week old ferrocyanide solution*

| $t$ | $a-x$ | K. $10^6$ |
|---|---|---|
| 0 | 20·10 | .. |
| 60 | 19·45 | 238 |
| 125 | 18·45 | 298 |
| 188 | 17·25 | 354 |
| 239 | 16·45 | 364 |
| 303 | 15·35 | 387 |

minutes and used after cooling. These results are recorded in Table III. The dark reaction was also studied by using ferrocyanide solution which had been kept in the dark for fifteen minutes after one hour's insolation by bright sunlight. These results are shown in Table IV.

TABLE III

*With pre-heated ferrocyanide solution*

| $t$ | $a-x$ | K. $10^6$ |
|---|---|---|
| 0 | 20·40 | .. |
| 60 | 19·80 | 215 |
| 120 | 18·70 | 315 |
| 180 | 17·10 | 426 |
| 240 | 15·90 | 451 |

TABLE IV

*With pre-insolated solution*

| $t$ | $a-x$ | K. $10^6$ |
|---|---|---|
| 0 | 20·30 | .. |
| 66 | 20·05 | 82 |
| 136 | 19·15 | 187 |
| 196 | 18·20 | 242 |
| 309 | 16·20 | 317 |

In all the experiments described above, the unimolecular velocity constants show a tendency to rise with the progress of the reaction. A freshly prepared solution of potassium ferrocyanide is distinctly a little more reactive than the one kept in the dark for a few days. A pre-heated solution also gives a distinctly lower dark reaction rate in the initial stage of the reaction. A much more pronounced diminution in the dark rate is brought about by using potassium ferrocyanide which had been kept in the dark for a few minutes after one hour's insolation. Thus in all these cases the velocity constants in the initial stages of the reaction are distinctly lower than those obtained with fresh ferrocyanide solutions.

The end products of this dark reaction are ferricyanide, alkali and part of the original ferrocyanide. It is well known that hydroxyl ions

accelerate the decomposition of hydrogen peroxide. In the presence of alkaline ferrocyanide the decomposition of hydrogen peroxide is considerably accelerated (Kassner, 1896),[17] (Quincke, 1897),[18] (Rupp., 1902),[19] (Sperber., 1913).[20] In fact, the reduction of ferricyanide by hydrogen peroxide in the presence of alkali has been used as a method for the estimation of ferrocyanide (Kassner, 1894),[21] (Quincke, 1891).[22]

The tendency of the unimolecular velocity constants to increase with the progress of the reaction is, therefore, to be attributed to the products of the reaction.

Although the decomposition of hydrogen peroxide is affected by the hydrogen-ion concentration, it is not practicable to keep it constant in the reaction under discussion, without affecting the rates of the dark decomposition and the photochemical after-reaction. The photochemical after-effect is dependent on the photo-formation of potassium aquopentacyanoferrite. The formation of the latter is accompanied by the appearance of alkali. In case the hydrogen-ion concentration is kept constant, this photo-equilibrium will be disturbed with the result that no photochemical after-effect may be detectable under certain conditions. Experiments to be reported later have shown that the rates of photochemical after-effect are much higher than the dark reaction rate in solutions containing a known amount of alkali (N/10 KOH) under otherwise identical conditions. Moreover, this reaction is highly susceptible to inhibitors, sensitizers and extraneous substances in general. Apart from disturbing the photochemical after-effect itself, the use of buffer solutions for keeping the hydrogen-ion concentration constant throughout the course of the reaction, is bound to introduce additional complications, thus rendering the investigation of the photochemical after-effect extremely difficult.

## BEHAVIOUR OF FERROCYANIDE SOLUTIONS IN THE DARK

Before the dark reaction between hydrogen peroxide and potassium ferrocyanide and the photochemical after-effect can be properly understood, it is necessary to study the properties of aqueous solution of ferrocyanide both in the dark and in light. The decomposition of aqueous ferrocyanide by light and air has been the subject of many investigations but the exact mechanism of the decomposition has not yet been elucidated.[23–31] Briggs[32] (1910) reported the existence of two stereoisomeric forms, $\alpha$- and $\beta$-ferrocyanide and remarked that solutions of the $\alpha$-salt upon prolonged standing are converted into the $\beta$-variety. Piutti[33] (1912), Hauser[34] (1912) and Wells[35] (1913), however, failed to establish any difference between the alleged varieties, and Bennett[36] (1917) concluded that the two forms are identical

crystallographically. The work of Kohltoff[30] (1920) showed no difference in the physical properties of solutions of $\alpha$- and $\beta$-ferrocyanide except their colour. It was later suggested by Briggs[37] (1920) that the supposed isomeride or $\beta$-variety consists of mixed crystals of potassium ferrocyanide and potassium aquopentacyanoferrite, the amount of latter being too small to detect by qualitative analysis. The amber colour of the crystals of ferrocyanide has been attributed to the presence of the aquo-salt (II), which is a strongly coloured substance. It has been suggested that the two compounds are in aqueous solution in a state of equilibrium.

$$K_4Fe(CN)_6 + H_2O \rightleftarrows K_3Fe(CN)_5H_2O + KCN \quad (I)$$

Acids increase the velocity of the reaction towards the right, alkalies to the left.

Iimori[38] has concluded on spectroscopic evidence that aqueous solutions of potassium ferrocyanide are gradually converted by heat, or hydrogen ions into potassium aquopentacyanoferrite in the dark. This evidence of the thermal formation of the aquo-salt from ferrocyanide supports the hypothesis of Briggs that in aqueous solution in the dark, potassium ferrocyanide is in equilibrium with the aquo-salt, the latter being present in quantities too small to be detected by qualitative analysis. The dependence of the stability of aqueous ferrocyanide on the hydrogen-ion concentration has also been established by Kohltoff and Pearson[39] (1931).

### Action of Light on Aqueous Ferrocyanide

The effect of light on aqueous ferrocyanide has been investigated by a large number of workers, with different results. According to Matuschek[40] (1901) solutions of ferrocyanide are gradually decomposed by light, with the formation of cyanide ions and precipitation of ferric hydroxide. Haber[41] (1905) and Foster[42] (1906) have concluded that under the influence of light ferrocyanide ion dissociates as follows:—

$$Fe(CN)_6'''' \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} Fe^{++} + 6\,CN'$$

The reaction is reversible, proceeding from right to left in the dark. Kassner[17] (1896) says that an alkaline solution of ferrocyanide hardly undergoes any decomposition when heated, and shows no change at all when exposed to light, except when air is included in the system. It has already been remarked that according to Weigert,[3] aqueous ferrocyanide produces reaction nuclei under the influence of light, while Winther[5] has remarked that the illumination of ferrocyanide results in the formation of an extremely stable substance. None of these workers could, however,

identify the product of insolation. Baudisch[43] (1921) observed that by illumination of freshly prepared aqueous solutions of ferrocyanide, an intense yellow colouration appears momentarily, but it gradually becomes deeper. This colouration does not appear in solutions which are dilute enough to be themselves colourless, and is much weaker, when oxygen-free ferrocyanide solution is illuminated *in vacuo*. The yellow colour was attributed to the formation of potassium pentacyanoperoxoferrite, $K_3Fe(CN)_5O_2$.

In a subsequent paper by Baudisch and Bass[44] (1922) this view was given up and it was stated that the citron yellow colour in air-free solution of ferrocyanide after illumination is not due to the peroxocompound. It was further concluded that the decomposition of ferrocyanide by light can take place in the absence of oxygen, which plays no part in the change of colour from light yellow to citron yellow. It was reported that a pale yellow alkaline solution of potassium ferrocyanide in water speedily becomes lemon yellow in colour when exposed to direct sunlight, but reverts to its original tint when placed in the dark. Only after some months, some ferrous hydroxide was precipitated. This view was again modified by Baudisch[45] (1929), and it was reported that ferrous ions, as well as pentacyanoaquoferrite ions are produced when solutions of potassium ferrocyanide, neutral or feebly acid, with carbonic acid, are exposed to the carbon arc or to direct sunlight in the absence of air. In the presence of air and light, the yellow ferrite ions are immediately oxidised to the dark violet pentacyanoaquoferrate ions which react with the first named ions to form complex compounds that have a pale yellow colour. This conclusion of Baudisch has, however, been found to be erroneous by the present author.

Rossi[46] and Bocchi (1925) observed that equilibrium conditions for a 0·25% solution of potassium ferrocyanide in water are reached after an exposure of thirty minutes to an arc. Complete reversibility of the reaction was shown after the first exposure to light and darkness, but with successive equal exposures the amount of decomposition increased and the reversibility of the reaction decreased. The decomposition was studied by measuring the alkalinity of the solution of the salt after exposure to sunlight. The reversibility of the reaction was investigated by alternately exposing to light and keeping in the dark a solution of the salt. According to Baur[47] (1925) solutions of potassium ferrocyanide darken in colour on illumination. If oxygen is led through the solution, the phenomenon is accentuated although darkening occurs also with carefully deaerated freshly prepared solutions. If the ferrocyanide solution is passed through a column of granulated aluminium, the original yellow colour disappears, and the solution ceases to be photochemically sensitive. These facts were inter-

preted as indicating that the ferrocyanide ion itself is photochemically insensitive, the light reaction being due to the photo-decomposition of the ferricyanide ion always present in small quantities.

Experiments conducted by the author with very dilute aqueous solutions of ferrocyanide both in air and under nitrogen in the total absence of oxygen have confirmed the observation that potassium aquopentacyanoferrite is produced photochemically and reversibly in the presence of light. Oxygen is not necessary for this photo-reaction. This was confirmed by tests with *para*-nitrosodimethylaniline[15] and nitrosobenzene.[16] Isobutyl alcohol is also a good reagent for demonstrating the influence of light on potassium ferrocyanide.[48] Exposed solutions of ferrocyanide ion gave unmistakable evidence for the presence of nitroprusside[49] (Hofmann) on the addition of small quantities of nitrite. The presence of aquopentacyano ferrite in aqueous ferrocyanide after momentary exposure to sunlight is, therefore, quite conclusive, and is in line with the spectroscopic evidence of Iimori.[38] The formation of aquopentacyanoferrite from ferrocyanide under the influence of light and hydrogen ions has been further established by Williams.[50]

The experiments described in this paper and the results reported on the properties of aqueous ferrocyanide solutions, show that the dark reaction between hydrogen peroxide and a pure aqueous freshly prepared solution of potassium ferrocyanide is really due to the action of the former on potassium aquopentacyanoferrite which exists as a substitution product (equation I) in quantities too small to be detected by qualitative analysis. The reaction between hydrogen peroxide and potassium cyanide is inappreciable, under the conditions of the experiments. The concentration of potassium aquopentacyanoferrite gradually diminishes on ageing, and the same effect is hastened by heat or prolonged insolation due to the decomposition of the former. It may be stated here that the suggestion of Baudisch[45] (1929) that in the presence of air, the pentacyanoaquoferrite formed on insolation of neutral ferrocyanide is oxidised to the dark violet pentacyanoaquoferrate, which reacts with the ferrocyanide to give more complex pale yellow compounds has been found to be untenable. Experiments conducted by the present author lead to the conclusion that the diminution in the concentration of potassium aquopentacyanoferrite on prolonged insolation of potassium ferrocyanide in experiments to be described later is really due to the decomposition of the former in the presence of air, light and alkali, and not due to its oxidation. In the presence of excess ferrocyanide, the violet aquo-salt is immediately reduced to the yellow aquo-salt, aquopentacyanoferrite. The same results have been arrived at by Williams[50] (1943),

## PHOTOCHEMICAL AFTER-EFFECT IN PRE-INSOLATED $H_2O_2$-$K_4Fe(CN)_6$ MIXTURE

The photochemical after-effect has been studied by exposing to sunlight (filtered through water) the reaction mixture for a definite period and studying the decomposition in the dark. It is well known that hydrogen peroxide is not sensitive to visible light[51] (Ellis and Wells, 1941) and the only reactant that is photosensitive to the visible part of the spectrum is potassium ferrocyanide. The photo-decomposition of hydrogen peroxide under the conditions of these experiments is, therefore, out of the question. Moreover the after-effect has been studied by measuring the decomposition of hydrogen peroxide in the dark after initial irradiation of the system. The photo-decomposition of hydrogen peroxide sensitised by ferrocyanide, if any, is, therefore, non-existent as soon as the system is brought in the dark.

In order to study the effect of wide variations in the period of pre-illumination of hydrogen peroxide-ferrocyanide mixtures, it was found necessary to use very low concentrations of potassium ferrocyanide so as to measure the rate of reaction conveniently. The low concentration of ferrocyanide has the added advantage in that the light effect is more marked than when stronger solutions are employed. With M/64·20 potassium ferrocyanide used in previous experiments by the author[1] (1939) and with long periods of pre-illumination by sunlight, the reaction was very violent and did not lend itself to accurate measurement. In the experiments mentioned here, therefore, M/320 potassium ferrocyanide and N/6 hydrogen peroxide were used with different periods of pre-illumination. In the following tables, 'T' stands for the time of pre-illumination of hydrogen peroxide-ferrocyanide mixture.

TABLE V

T = ½ mt.

| $t$ | $a-x$ | K. $10^5$ |
|---|---|---|
| 0 | 20·10 | .. |
| 18 | 16·30 | 506 |
| 42 | 12·10 | 525 |
| 55 | 10·35 | 524 |
| 75 | 8·20 | 520 |
| 100 | 6·00 | 526 |

TABLE VI

T = 1 mt.

| $t$ | $a-x$ | K. $10^5$ |
|---|---|---|
| 0 | 17·80 | .. |
| 6 | 16·50 | 548 |
| 13 | 15·10 | 549 |
| 26 | 12·70 | 564 |
| 36 | 11·20 | 559 |
| 47 | 9·85 | 547 |
| 58 | 8·00 | 599 |
| 68 | 6·95 | 601 |

TABLE VII

T = 3 mts.

| $t$ | $a-x$ | K. $10^5$ |
|---|---|---|
| 0 | 16·20 | .. |
| 5 | 14·90 | 726 |
| 11 | 13·40 | 749 |
| 19 | 11·80 | 724 |
| 27 | 10·40 | 713 |
| 37 | 8·90 | 703 |
| 50 | 6·90 | 741 |
| 65 | 5·15 | 766 |

TABLE VIII

T = 5 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 14·30 | .. |
| 5 | 12·90 | 894 |
| 10 | 11·70 | 871 |
| 15 | 10·70 | 839 |
| 25 | 8·65 | 873 |
| 38 | 6·70 | 866 |
| 50 | 5·20 | 879 |
| 62 | 4·00 | 892 |

TABLE IX

T = 8 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 11·75 | .. |
| 5·5 | 10·20 | 1120 |
| 14·5 | 8·25 | 1060 |
| 28 | 5·95 | 1060 |
| 43·5 | 4·05 | 1060 |
| 78 | 1·40 | 1190 |

TABLE X

T = 10 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 11·00 | .. |
| 4·5 | 9·70 | 1214 |
| 11·5 | 8·05 | 1180 |
| 19·5 | 6·40 | 1207 |
| 32 | 4·50 | 1213 |
| 55 | 2·40 | 1202 |

TABLE XI

T = 15 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 7·70 | .. |
| 5 | 6·50 | 1468 |
| 12 | 5·10 | 1490 |
| 25·25 | 3·35 | 1432 |
| 54 | 1·30 | 1430 |

In these experiments the magnitude of the photochemical after-effect has been determined by subtracting from the total rate, the rate of the dark reaction (Table I, $K \times 10^5 = 35$, average value).

Though the velocity constants obtained here leave something to be desired, they are as good as those reported in the literature [Kistiakowsky,[2] Bredig[52] (1899), (1901), Brossa[53] (1909), Tartar and Schaffer[54] (1928)].

This effect of pre-illumination of the reaction mixture on the magnitude of the photochemical after-effect as measured by the velocity constants has been illustrated in the figure. The effect of the dark reaction has been eliminated, as already stated, by subtracting from the observed rate, the rate of the dark reaction, thus determining the magnitude of the photochemical after-effect.

Experiments performed by using light from a 500-watt gas-filled filament lamp operated on 220 volts are recorded in Tables XII to XV.

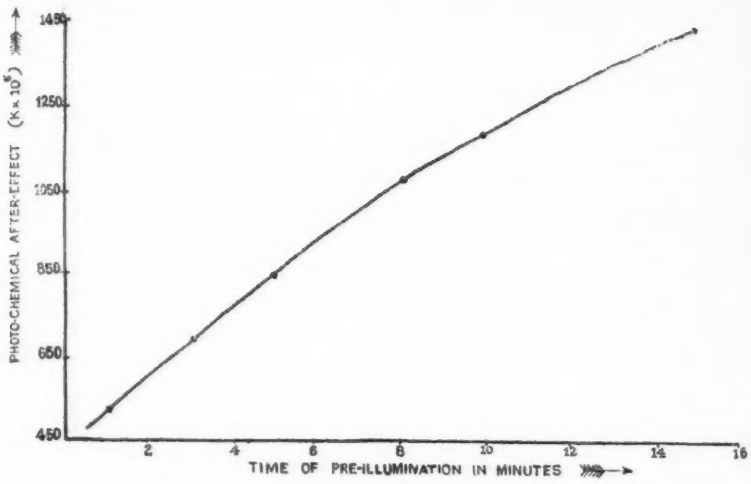


FIG. 1

The velocity constants above the line in Tables XII–XV represent the values for the light reaction.

It is seen from these results that the photochemical after-effect is more marked, the greater the period of pre-illumination of the mixture. The dark equilibrium in aqueous ferrocyanide with the formation of a trace of aquopentacyanoferrite is shifted further to the right on illumination with increased concentration of aquo-ferrite. The latter causes the enhanced rate of decomposition of hydrogen peroxide on subsequent darkening, resulting in the marked photochemical after-effect. In the presence of

TABLE XII

T = 5 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 20·05 | .. |
| 5 | 19·90 | 64 |
| 15 | 19·50 | .. |
| 49 | 18·00 | 70 |
| 122 | 16·30 | 73 |
| 180 | 14·90 | 71 |
| 278 | 12·00 | 80 |
| 400 | 9·90 | 77 |

TABLE XIII

T = 15 mts.

| $t$ | $a - x$ | K. $10^5$ |
|---|---|---|
| 0 | 20·45 | .. |
| 15 | 19·40 | 15 |
| 25 | 18·60 | .. |
| 69 | 15·75 | 164 |
| 129 | 12·85 | 154 |
| 192 | 10·35 | 153 |
| 310 | 7·40 | 141 |
| 434 | 5·40 | 131 |

TABLE XIV

T = 30 mts.

| $t$ | $a-x$ | K. $10^5$ |
|---|---|---|
| 0 | 20·35 | .. |
| 30 | 17·55 | 211 |
| 40 | 16·80 | .. |
| 80 | 13·75 | 217 |
| 120 | 10·90 | 235 |
| 180 | 7·80 | 238 |
| 261 | 5·20 | 231 |
| 360 | 3·10 | 229 |

TABLE XV

T = 42 mts.

| $t$ | $a-x$ | K. $10^5$ |
|---|---|---|
| 0 | 20·60 | .. |
| 42 | 15·80 | 310 |
| 52 | 15·40 | .. |
| 91 | 11·65 | 310 |
| 123 | 9·20 | 315 |
| 157 | 7·00 | 326 |
| 219 | 4·45 | 323 |
| 287 | 2·60 | 329 |

hydrogen peroxide the photo-equilibrium continues to shift to the right with the formation of increasing amounts of aquopentacyanoferrite. This explains why on the cessation of illumination, the velocity constants are higher, the longer the exposure.

## SUMMARY

The dark reaction between hydrogen peroxide and a pure dilute aqueous solution of potassium ferrocyanide has been critically examined. The experiments described in the paper lead to the conclusion that potassium aquopentacyanoferrite produced as a substitution product in very minute concentration in aqueous ferrocyanide in the dark reacts with hydrogen peroxide resulting in the measured dark reaction. Aged solutions of ferrocyanide, as well as pre-heated and pre-illuminated solutions used sometime after treatment show a distinctly lower rate of peroxide decomposition. This diminished reactivity towards hydrogen peroxide appears to be due to the partial decomposition of the aquo-complex salt by heat, prolonged exposure to light and ageing.

The marked photochemical after-effect observed in the pre-insolated mixture of hydrogen peroxide and potassium ferrocyanide has been studied in detail with varying periods of pre-illumination of the reaction mixture. It is found that the greater the period of pre-illumination of the mixture, the greater is the photochemical after-effect within the concentration limits of reactants used in the experiments.

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# OXIDATION OF ETHANOL UNDER SILENT ELECTRIC DISCHARGE

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Vapour phase—catalytic[1] and thermal—studies in the behaviour of ethanol have resulted in establishing processes for the manufacture of industrially important substances like ethylene, acetaldehyde, acetone, ether, acetic acid, acetic anhydride, ethyl acetate and many other related or derived products; a review of the rather considerable literature, however, indicated that very little work has been carried out on this substance under electrical excitation.[2–6] Since (i) discharge reactions are analogous, at least in some measure, to high temperature reactions and (ii) most of the above mentioned substances are oxidation products of alcohol, an oxidative study using air under silent electric excitation has been undertaken. The present paper records some general findings.

## Apparatus and Experimental Procedure

The experimental procedure consisted essentially in bubbling air at a suitable rate through alcohol maintained at a particular temperature and allowing the air-alcohol vapour mixture thus formed to pass through the annular space of a Siemens' all glass ozonizer subjected to a high voltage A.C. discharge. The effluent gases were scrubbed off their soluble constituents by passing them through a series of water wash-traps. The washings were examined and analysed for the possible products formed.

The apparatus consisted of a train of the following fixtures: (*a*) An air bubbler F, for aeration of alcohol vapours, (*b*) the reaction vessel O, (*c*) the wash traps W, (*d*) a flow meter M, for measuring the rate of flow of gases and (*e*) a vacuum pump C, for producing suction. The arrangement together with the electrical circuit is shown in Fig. 1: F is a round-bottom flask of about 200 c.c. capacity containing ethyl alcohol of any desired concentration; it can be maintained at a constant temperature with the help of the surrounding water-bath B. The F is fitted with two delivery tubes one dipping under the surface of the alcohol for drawing in air and the other,

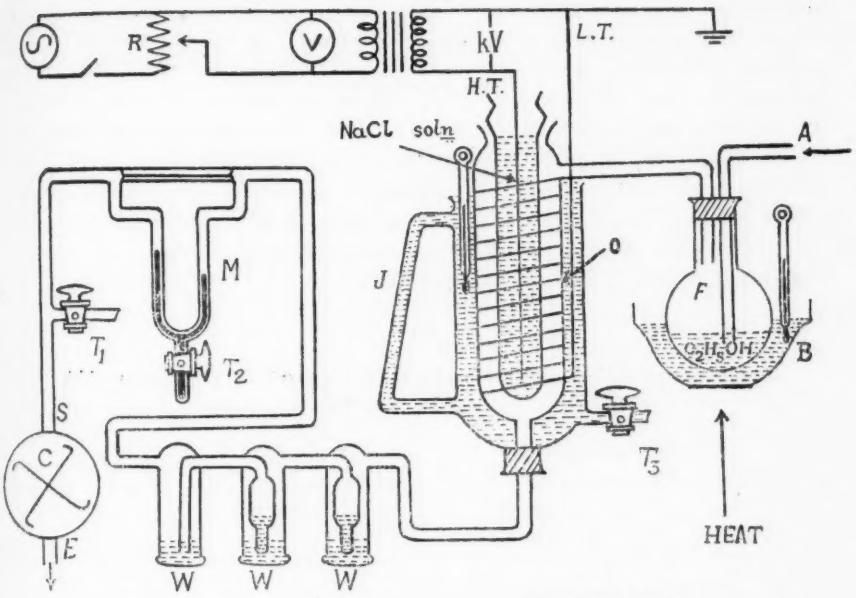


FIG. 1. Oxidation of Ethyl Alcohol under Silent Electric Discharge.

the shorter one which served as the outlet for the air-alcohol mixture. The outlet is connected to the discharge tube O which is provided with leads for letting the gases in and out respectively. The O is a simple Siemens' type all glass ozonizer; it is surrounded by a water jacket (J) with a side loop for heating it when necessary and with leads for circulating water. Either by heating the jacket or by circulating water through it, the temperature of the ozonizer could be maintained as required. The ozonizer is followed by three wash-traps (W) connected in series containing distilled water for washing the effluent gases. These are followed by a flow meter (M) and a 'Cenco' hyvac pump (C). The difference in the levels of two mercury columns of the former gives the rate of flow of the gases. This last could be controlled with the help of the stop cock $T_1$ and by adjusting the speed of the pump by a rheostat.

For every experiment a known quantity of aqueous ethyl alcohol of desired concentration was taken in the flask F which was maintained at a constant temperature. Air was sucked in through this at a uniform rate under a constant head maintained with the help of the flow-meter, its stop-cocks and the rheostat controlling the speed of the pump. By independent

experiments the flow-meter was calibrated for the volume of air sucked in a unit time under different heads of mercury column. Duration of an experiment was generally 4 hours exposure to discharge at the end of which the residual ethyl alcohol was assayed (by finding out the sp. gr. and thence the amount in gm.) and the liquor from wash traps collected and estimated for formaldehyde, acetaldehyde, formic acid and acetic acid, since these only happened to be formed in measurable quantities. Experiments were carried out with respect to (i) the temperature of alcohol, (ii) concentration of alcohol, (iii) applied potential and (iv) frequency of the A.C. supply. Results are presented in Tables I, II, and III.

TABLE I

*Oxidation of Ethyl Alcohol under Silent Electric Discharge (at 500 Cycles of A.C.): Influence of Applied Potential*

| | |
|---|---|
| Transformer ratio | 1 : 195 |
| Duration of discharge | 4 hours |
| Amount of alcohol taken | 30 c.c. (80·5% by wt.) |
| Temperature of alcohol | 50° |
| Air passed | 385 c.c./minute |
| Temperature of the ozonizer | 30° C. |
| Absorbers | 3 in series |
| Alcohol consumed | 4 gm. |

| No. | Applied potential | Products* | | | | Total conversion % |
|---|---|---|---|---|---|---|
| | | Aldehyde yield | | Acid yield | | |
| | | HCHO g. | $CH_3CHO$ g. | H·COOH g. | $CH_3COOH$ g. | |
| 1 | 5·85 | 0·021 | Nil | Nil | 0·013 | 0·8 |
| 2 | 6·24 | 0·099 | 0·115 | 0·093 | 0·161 | 11·7 |
| 3 | 6·63 | 0·034 | 0·332 | 0·163 | 0·226 | 20·1 |
| 4 | 7·02 | 0·077 | 0·321 | 0·100 | 0·208 | 17·7 |
| 5 | 7·41 | 0·046 | 0·770 | 0·319 | 0·233 | 34·2 |

* Three bubblers were connected in series for the absorption of products. Independent experiments indicated that the absorption was complete in the first two bubblers. The third bubbler served as a safety device.

Gas analysis of the possible gaseous products was not carried out because they are mixed with a overwhelmingly large quantity of unused air.

TABLE II

*Oxidation of Ethyl Alcohol under Silent Electric Discharge (at 50 Cycles of A.C.): Influence of Applied Potential*

| | |
|---|---|
| Transformer ratio .. .. | 1 : 133 |
| Amount of alcohol taken .. | 30 c.c. (80·5% by wt.) |
| Temperature of alcohol .. .. | 40° C. |
| Air passed .. .. .. | 384 c.c./minute |
| Duration of discharge .. .. | 4 hours |
| Absorbers .. .. .. | 3 in series |
| Alcohol consumed .. .. | 3·2 to 3·5 gm. |
| Temperature of ozonizer .. | 30° C. |

| No. | Applied potential kV | Products | | | | Total conversion % |
|---|---|---|---|---|---|---|
| | | Aldehydes | | Acids | | |
| | | H·CHO g. | $CH_3CHO$ g. | H·COOH g. | $CH_3$·COOH g. | |
| 1 | 7·45 | 0·026 | Nil | 0·004 | 0·014 | 1·3 |
| 2 | 9·04 | 0·044 | 0·001 | 0·006 | 0·017 | 2·1 |
| 3 | 9·31 | 0·069 | 0·022 | 0·011 | 0·038 | 4·2 |

Influence of potential on the decomposition of ethyl alcohol and formaldehyde were also investigated independently. These results are shown in Tables IV and V.

*Procedure of Estimating Acetaldehyde, Formaldehyde, Acetic Acid and Formic Acid in the Products*

An analysis of the liquors from the wash traps indicated the presence mainly of formaldehyde, acetaldehyde, formic acid and acetic acid. The total aldehyde was first determined by the bisulphite method[7, 8] and formaldehyde by Romijn's potassium cyanide method[9, 10]. Quantity of acetaldehyde was obtained by difference from these two.

In a given aliquot of the washings (say 20 c.c.) total acid was determined by titration with a standard decinormal alkali using phenolphthalein as indicator. This solution was then boiled to expel all the aldehydes and sodium acetate and a few c.c. of a 5% mercuric chloride added and solution maintained near boiling temperature for about 20 minutes. It was then cooled and filtered and the filtrate again titrated with decinormal alkali. This second titre value gave the amount of formic acid.[11, 12] Acetic acid was calculated by difference.

TABLE III

*Oxidation of Ethyl Alcohol under Silent Electric Discharge: Influence of Temperature and Alcohol Concentration*

Alcohol taken .. .. .. 100 c.c. solution
Air passed .. .. .. 385 c.c./minute
Frequency of A.C. supply .. 500 cycles/sec.
Transformer ratio .. .. 1 : 195
Duration of discharge .. .. 4 hours
Applied potential .. .. 6·24 kV (r.m.s.)
Absorbers .. .. .. 3 in series
Temperature of the Ozonizer .. 30° C.

| No. | Alcohol concentration % | Temp. of the alcohol* °C. | Alcohol consumed g. | Products | | | | Total conversion % |
|---|---|---|---|---|---|---|---|---|
| | | | | Aldehydes | | Acids | | |
| | | | | H.CHO g. | $CH_3$.CHO g. | H.COOH g. | $CH_3COOH$ g. | |
| 1 | 10 | 25 | 3·4 | 0·029 | 0·006 | 0·034 | 0·094 | 4·7 |
| 2 | 10 | 41 | 3·9 | 0·094 | 0·005 | 0·031 | 0·121 | 6·3 |
| 3 | 10 | 50 | 4·68 | 0·111 | 0·003 | 0·029 | 0·144 | 8·1 |
| 1 | 20 | 31 | 4·4 | 0·087 | 0·003 | 0·052 | 0·138 | 6·3 |
| 2 | 20 | 41 | 5·3 | 0·090 | 0·008 | 0·033 | 0·096 | 4·3 |
| 3 | 20 | 50 | 6·36 | 0·107 | 0·097 | 0·054 | 0·129 | 6·1 |

* Although the temperature of the alcohol was higher than that of the ozonizer in certain of these experiments (and also in Tables I and II) there was no perceptible condensation of alcohol on the ozonizer sides. This must be due to the high rate at which the air was flowing which did not get saturated with respect to alcohol vapour.

## DISCUSSION OF THE RESULTS

It will be seen from Table I that at 5·85 kV, the threshold potential at 500 cycles, the yields of all the products are very low, the total conversion being less than 1% on the basis of the alcohol used up. At potentials above the threshold (5·85 to 7·41 kV), the total conversion of alcohol has increased from 0·8% to 34·2%. Although the absolute yield as well as the percentage yield of formaldehyde calculated on the basis of total conversion, goes on falling with increasing applied potentials, the formation of other products, *viz.*, acetaldehyde, formic acid and acetic acid has been greatly augmented: Acetaldehyde has increased from 0·115 gm. to 0·770 gm., almost seven

TABLE IV

*Decomposition* of Streaming Formaldehyde Vapour under Silent Electric Discharge (A.C. 500 Cycles) at 30° and at 60 mm. Hg*

| Applied potential kV | Duration of discharge hr. | Gas collected c.c. | Analysis of the products | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $CO_2$ % | Unsat. hydrocarbon % | $O_2$ % | CO % | $CH_4$ % | $H_2$ % |
| 1·57 | 3 | 35 | 5·7 | 2·0 | 6·6 | 12·8 | 25·2 | 55·2 |
| 1·95 | 1½ | 25 | 4·0 | 3·2 | 3·2 | 11·6 | 14·4 | 72·0 |
| 2·84 | 3 | 30 | 10·0 | 3·3 | 3·3 | 13·3 | 9·3 | 63·5 |
| 2·91 | 3 | 35·5 | 12·7 | 1·4 | 6·5 | 11·8 | 8·0 | 75·2 |
| 3·90 | ½ | 21·3 | 11·0 | 2·8 | 2·8 | 10·7 | 8·2 | 70·2 |

TABLE V

*Decomposition* of Streaming Ethyl Alcohol Vapour under Silent Discharge (A.C. 500 Cycles) at 30° and at 78 mm. Hg*

| Applied potential kV | Duration of discharge hr. | Gas collected c.c. | Analysis | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $CO_2$ % | Unsat. hydrocarbon % | $O_2$ % | CO % | $H_2$ % | $CH_4$ % | $C_2H_6$ % |
| 2·34 | 3 | 52·6 | 2 | 2 | 3·9 | 3·9 | 21·3 | 5·3 | 52 |
| 3·51 | 1½ | 29·4 | 4·8 | 3·4 | 3·4 | 6·8 | 46·7 | 25 | 13·3 |

* In absence of oxygen.

folds; yield of formic acid has been trebled and of acetic acid increased by about 50% (*vide* Table I, columns 3, 4, 5, 6 and 7).

In Table II are presented the results of similar experiments at 50 cycles of A.C. discharge. As will be seen, compared to 500 cycles, the formation of various products has been very poor; the total conversion being 1·3, 2·1 and 4·2% of alcohol vapour at 7·45, 9·04 and 9·31 kV respectively. In these experiments, however, although the trend of the yields of acetaldehyde, formic acid and acetic acid is similar to that at 500 cycles (*vide* Table I), the formation of formaldehyde appears to have been favoured by

increasing applied potentials and is generally much greater when expressed as percentage of the total conversion. For example in Table I, the maximum yield of formaldehyde is 0·099 gm. at 6·24 kV when the total conversion is 11·7%, whereas in Table II, 0·044 and 0·069 gm. are obtained at 2·1% and 4·2% total conversion respectively. In addition, since the experiments in Table II were conducted at a lower temperature (40°) of alcohol, less of this last was used (3·2–3·5 gm.) as compared to that in experiments at 500 cycles (4 gm.). These results suggest therefore, that for oxidation products other than formaldehyde, discharge at high potentials of 500 cycles gives better yields; formaldehyde formation, on the other hand, is favoured at high potentials of 50 cycles discharge.

Results in Table III are suggestive in regard to the influence of alcohol vapour–air ratio. In the present experiments, increased concentration of alcohol vapours in the discharge tube obtained by increasing the temperature or concentration of alcohol, for a given rate of air flow, has not materially influenced the yields of various products, though a slightly favourable trend is perceptible. This may be (i) due to saturation with respect to the capacity of the discharge tube or (ii) due to limiting influence of the proportion of air obtaining in these experiments.

## MECHANISM OF THE REACTIONS

It is evident from the results that there is a direct parallelism in the quantities of acetic acid and acetaldehyde formed (Table I). There can be little doubt, therefore, that the latter is an intermediate stage in the formation of the former. Further, since all the factors excepting the applied potential are constant and increase in this last is favourable to ozone formation[13] or augmented excitation of oxygen molecules, it is very likely that these two substances are formed as a result of direct oxidation in the gas phase.

The yield of formaldehyde has gradually decreased and that of formic acid increased with increasing applied potential (Table I). The fall in the yield of the former is probably due (i) to its increased oxidation to formic acid and (ii) to decomposition (*vide* Table IV) which is found to be greater at higher applied potentials.

While the formation of acetaldehyde and acetic acid is understandable as products of direct oxidation of ethyl alcohol, the formation of formaldehyde and formic acid is not quite so easily explicable. There are two or three possible modes by which the former may arise. As for formic acid, from the observed data it is evident that formaldehyde is most probably an intermediate in its formation.

Bone and Stockings[14] observed the formation of formaldehyde in thermal oxidation of acetaldehyde:

$$CH_3 \cdot CHO \xrightarrow{O} CH_2OH \cdot CHO \xrightarrow{O} CO + H \cdot CHO + H_2O.$$

Bone and co-workers[15] showed that ethylene which can arise from ethyl alcohol also gives formaldehyde. They formulated the change as:

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow{O} \begin{matrix} CH_2 \\ \| \\ CH \cdot OH \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \xrightarrow{O} \begin{matrix} CH \cdot OH \\ \| \\ CH \cdot OH \end{matrix} \rightarrow 2\,HCHO$$

$$\xrightarrow{O} H \cdot COOH + CO + H_2O + CO_2$$

$$\xrightarrow{O} \begin{matrix} CH_2 \cdot OH \\ | \\ COOH \end{matrix} \rightarrow HCHO + CO + H_2O.$$

On the basis of additional evidence of the formation of acetaldehyde from ethylene, Blair and Wheeler[16] modified the above mechanism:

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow{O} \begin{matrix} CH_2 \\ \| \\ CH \cdot OH \end{matrix} \rightarrow \begin{matrix} CH_3 \\ | \\ CHO \end{matrix} \xrightarrow{O} \begin{matrix} CH_2 \cdot OH \\ | \\ CHO \end{matrix} \rightarrow 2\,HCHO.$$

Unpublished work of the authors has also shown that acetaldehyde vapour can be directly oxidized to formaldehyde, although the latter is formed in traces only.

From the observed data (Table I), however, it is fairly certain in the present case that acetaldehyde is not an intermediate stage in the main reaction giving rise to formaldehyde. Ethylene is known to be formed[17–20] under a variety of conditions from ethyl alcohol but in the present conditions the quantity is not sensible and it does not show any material increase on increasing the applied potential (Table V). It is not therefore, an intermediate in the formation of acetaldehyde or/and formaldehyde.

From Table V it is apparent that ethane and methane are formed in considerable quantities by the decomposition of ethanol under the conditions obtained in the experiments reported. It appears quite probable that formaldehyde arises by the oxidation of these through free methyl radicals,[21–23] which are formed under electrical excitation not only from methane and ethane but also from ethyl alcohol.

Further work is in progress to study the various other aspects of the reaction.

Sincere thanks of the authors are due to Professor S. S. Joshi, D.Sc., for his keen interest in the progress of the work and valuable criticism.

## SUMMARY

Alcohol vapour–air mixtures obtained by bubbling air under a pressure of 7 cm. Hg through alcohol of different concentrations, were subjected to an A.C. discharge of 500 and 50 cycles in a Siemens' ozonizer for a duration of 4 hours. The main products formed were acetaldehyde, acetic acid, formaldehyde and formic acid which were absorbed in water and estimated. Influence of applied potential varied in the range 5·85 to 7·41 kV, of supply frequencies, *viz.*, 50 and 500 cycles and alcohol concentration and temperature was investigated. Formaldehyde increased to a maximum of 0·099 gm. at 6·24 kV and decreased thereafter. The formation of acetaldehyde, acetic acid and formic acid was favoured by increasing potentials. The yields at 50 cycles were generally very poor with respect to products other than formaldehyde. At 7·41 kV of 500 cycles highest conversion of alcohol, to the extent of 34% was noticed.

Mechanism of the reactions has been discussed and it is suggested that formaldehyde arises by the oxidation of free methyl radicals.


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# RING FREQUENCIES OF DIOXANE AND TRIOXANE

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## Introduction

The vibrational frequencies of a molecule may be calculated by writing the kinetic and potential energies with the help of cartesian displacement symmetry co-ordinates. This method is very laborious, and much time may be saved if we use the matrix method described by Wilson.[1] In the present investigation we have calculated the ring frequencies of dioxane and trioxane molecules by this method which is briefly described below.

We first write the internal symmetry co-ordinates ($R_j$) corresponding to each class of the point group in terms of the internal co-ordinates ($r_k$) which are the changes of bond lengths and bond angles. There are of the form $R_J = \sum_k U_{Jk} r_k$. In matrix notation we may write $\mathbf{R} = \mathbf{Ur}$ where $\mathbf{R}$ is the column matrix $(R_1, R_2 \ldots R_n)$ and $\mathbf{r}$ is the column matrix $(r_1, r_2, r_3 \ldots r_n)$ and $\mathbf{U}$ is the normalised transformation matrix.

The potential energy in terms of the internal co-ordinates ($r_k$) is given by $2V = \sum_{ik} f_{ik} r_i r_k$, where $f_{ik}$ are the force constants ($f_{ik} = f_{ki}$) and $i, k$ extend over all the internal co-ordinates. It can also be expressed in terms of internal symmetry co-ordinates ($R_j$) by $2V = \sum_{Jl} F_{Jl} R_J R_l$, where $F_{Jl} = F_{lJ}$ and J and $l$ extend over all internal symmetry co-ordinates. In matrix form we may write $2V = \mathbf{r'fr} = \mathbf{R'FR}$, where $\mathbf{f}$ and $\mathbf{F}$ are symmetric matrices and $\mathbf{r'}$ and $\mathbf{R'}$ are the transposes of $\mathbf{r}$ and $\mathbf{R}$ matrices.

With the help of the inverse transformation $\mathbf{r} = \mathbf{U^{-1}R}$, where $\mathbf{U^{-1}}$ is the inverse matrix of $\mathbf{U}$ and since $\mathbf{U^{-1}} = \mathbf{U'}$ as $R_i$'s are orthogonal and normalised, we get $\mathbf{r} = \mathbf{U'R}$. Therefore $\mathbf{r'} = (\mathbf{U'R})' = \mathbf{R'U}$ since the transpose of a product is equal to the product of the transposes taken in reverse order. We get then $2V = \mathbf{R'Uf\,U'R} = \mathbf{R'FR}$ so that $\mathbf{F} = \mathbf{UfU'}$ which gives the F matrix.

The elements of the $\mathbf{f}$ and $\mathbf{U}$ matrices are easily known and with their help the elements of the $\mathbf{F}$ matrix can be written down.

Since $r_k = \sum_{i=1}^{3n} B_{ki} x_i$, where $r_k$ is the $k$th internal co-ordinate and $x_i$ is the $i$th cartesian co-ordinate among the $3n$ cartesian displacement co-ordinates of the $n$ atoms, we can consider $B_{ki}$'s as components of a vector $\mathbf{s}_{kt}$ and $x_i$ as components of a vector $\boldsymbol{\rho}_t$ both belonging to atom $t$ so that

$$r_k = \sum_{t=1}^{n} \mathbf{s}_{kt} \cdot \boldsymbol{\rho}_t$$

The kinetic energy in terms of the internal co-ordinates may be written as $2T = \Sigma g_{kk'} p_k p_{k'}$, where the $p_k$'s are momenta conjugate to internal co-ordinate $r_k$ and

$$g_{kk'} = \sum_{i=1}^{3n} \mu_i B_{ki} B_{k'i} = \sum_{t=1}^{n} \mu_t \mathbf{s}_{kt} \cdot \mathbf{s}_{k't}$$

where $\mu_t$ is the reciprocal of the mass of the $t$ atom.

In matrix notation $2T = \mathbf{p'gp}$.

If **P** be the momentum matrix for the internal symmetry co-ordinate ($R_J$) and **p** for the we internal co-ordinate ($r_k$) we have $\mathbf{P} = \mathbf{Up}$ and the kinetic energy matrix can be written as $2T = \mathbf{P'UgU'P} = \mathbf{P'GP}$ which gives the **G** matrix.

The elements of the **G** matrix are found with the help of the $\mathbf{s}_{kt}$ vectors, where $t$ refers to the atom and $k$ to the internal co-ordinate ($r_k$). These can be expressed in terms of unit vectors directed along chemical bonds. If **V'** denotes the unit vector along the bond from atom $t$ to atom $t'$ (Fig. 1) then

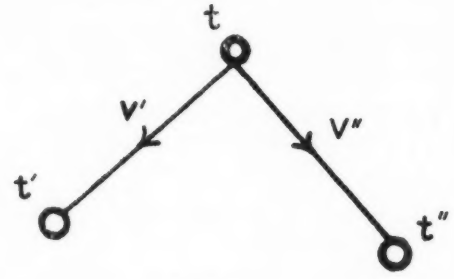


FIG. 1

$\mathbf{s}_{kt} = -\mathbf{V'}$ and $\mathbf{s}_{kt'} = \mathbf{V'}$. If we have a third atom $t''$ and the unit vector along $tt''$ is $\mathbf{V''}$ then the $\mathbf{s}_{kt}$ vectors associated with the change of inter-bond angle $\phi$ are

$$\mathbf{s}_{kt'} = \frac{\mathbf{V'}\cos\phi - \mathbf{V''}}{\sin\phi} \epsilon \text{ and } \mathbf{s}_{kt''} = \frac{\mathbf{V''}\cos\phi - \mathbf{V'}}{\sin\phi} \tau$$

for the end atoms $t'$ and $t''$ and

$$s_{kt} = [(T - \epsilon \cos \phi)\, V' + (\epsilon - T \cos \phi)\, V''] \frac{1}{\sin \phi}$$

for the apex atom '$t$', where $\epsilon$ and T are the reciprocal of the bond lengths $tt'$ and $tt''$.

Therefore if $G_{ll'}$ be an element of matrix **G**

$$G_{ll'} = \sum_p \mu_p n_p \sum_{kk'} U_{lk} U_{l'k'} s_{k't'} \cdot s_{kt}$$

If we define **S** vectors by the transformation $S_j^{(t)} = \sum_k U_{jk} s_{kt}$, where $j$ refers to the $j$th internal symmetry co-ordinate, $t$ to $t$th atom, and $U_{lk}$'s are the corresponding elements of the **U** matrix;

$$G_{ll'} = \sum_p \mu_p n_p S_l^{(t)} \cdot S_{l'}^{(t)} \text{ where } l \text{ and } l'$$

refer to the internal symmetry co-ordinates, $p$ refers to a set of equivalent atoms, a typical one of the set being $t$, $\mu_p$ is the reciprocal of the mass of the typical atom $t$ and $n_p$ is the number of equivalent atoms in the $p$th set and the summation extends over all the sets of equivalent atoms in the molecule. The above expression is true for non-degenerate vibrations only. For the degenerate ones we have

$$G_{ll'} = \frac{1}{c} \sum_p \mu_p n_p (S_{la}^{(t)} \cdot S_{l'a}^{(t)} + \ldots + S_{lc}^{(t)} \cdot S_{l'c}^{(t)})$$

where $c$ is the degree of degeneracy.

The secular equation can be formed from the expressions for the kinetic and potential energies

$$2V = \sum_{ij} F_{ij} R_i R_j \text{ and } 2T = \sum_{ij} G_{ij} P_i P_j,$$

where $F_{ij}$ and $G_{ij}$ are the elements of **F** and **G** matrices and $R_i$ and $P_i$ of the **R** and **P** matrices.

Using Hamilton's equations of motions $R_i = \frac{\partial H}{\partial P_i}$ and $P_i = -\frac{\partial H}{\partial R_i}$, where $H = T + V$, it is seen that two equivalent forms of the secular equation are

$$|\mathbf{FG} - \omega^2 \mathbf{E}| = 0 \text{ or } |\mathbf{GF} - \omega^2 \mathbf{E}| = 0,$$

where **E** is a unit matrix, $\omega = 2\pi\nu$, where $\nu$ is the frequency, and **F** and **G** are the matrices discussed above.

## 2. Calculation of Frequencies for the Dioxane Ring

According to the electron diffraction data of Sutton and Brockway,[2] the molecule exists predominantly in the chair form, the length of the

C–C bond = 1·54 Å, of the C–O bond = 1·46 Å ± 04 Å and the oxygen bond angle 110° ± 5°. For our calculations we have taken all the bond angles to be 109° 28′. The molecule belongs to the point group $C_{2h}$ and the character table is given in Table I.

TABLE I

| $C_{2h}$ | E | $C_2^x$ | $i$ | $\sigma_x$ | $n_i$ | Selection rule | |
|---|---|---|---|---|---|---|---|
| | | | | | | R | I R |
| $A_g$ | 1 | 1 | 1 | 1 | 4 | pol. | $f$ |
| $A_u$ | 1 | 1 | −1 | −1 | 3 | $f$ | $a$ |
| $B_g$ | 1 | −1 | 1 | −1 | 2 | dep. | $f$ |
| $B_u$ | 1 | −1 | −1 | 1 | 3 | $f$ | $a$ |

$n_i$ is the number of internal vibrations.

The molecule is as shown in Fig. 2.

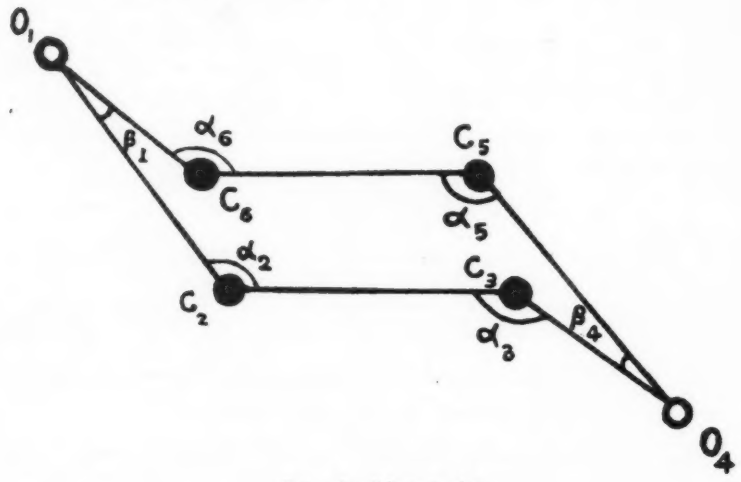


FIG. 2. Dioxane ring.

The $x$-axis is the axis of twofold symmetry and lies in the plane $C_2C_3C_5C_6$. If $r_{ij}$ and $d_{ij}$ are the changes in the length of the valence bonds between the carbon and oxygen atoms (C–O) and between the carbon-carbon

atoms (C–C) respectively and $\alpha_i$ and $\beta_i$ represent the changes of bond angles at the $i$th atom for the carbon and oxygen atoms respectively the internal symmetry co-ordinates for the various classes are:

Class $A_g$

$$R_1 = \tfrac{1}{2}(r_{12} + r_{34} + r_{45} + t_{61})$$

$$R_2 = \frac{1}{\sqrt{2}}(d_{23} + d_{56})$$

$$R_3 = \tfrac{1}{2}(\alpha_2 + \alpha_3 + \alpha_5 + \alpha_6)$$

$$R_4 = \frac{1}{\sqrt{2}}(\beta_1 + \beta_4)$$

Class $A_u$

$$R_1 = \tfrac{1}{2}(r_{12} + r_{34} - r_{45} - r_{61})$$

$$R_2 = \frac{1}{\sqrt{2}}(d_{23} - d_{56})$$

$$R_3 = \tfrac{1}{2}(\alpha_2 + \alpha_3 - \alpha_5 - \alpha_6)$$

Class $B_g$

$$R_1 = \tfrac{1}{2}(r_{12} - r_{34} + r_{45} - r_{61})$$

$$R_2 = \tfrac{1}{2}(\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$$

Class $B_u$

$$R_1 = \tfrac{1}{2}(r_{12} - r_{34} - r_{45} + r_{61})$$

$$R_2 = \tfrac{1}{2}(\alpha_2 - \alpha_3 - \alpha_5 + \alpha_6)$$

$$R_3 = \frac{1}{\sqrt{2}}(\beta_1 - \beta_4)$$

If $\mu_O$ is the reciprocal of the mass of O atoms

$\mu_{CH_2}$ ,, ,, ,, $CH_2$ group

$\epsilon$ ,, ,, ,, ,, bond length between C and O atoms

$\tau$ ,, ,, ,, ,, ,, ,, C and C atoms

$f_r$ is the force constant of C–O valence

$f_d$ ,, ,, ,, C–C ,,

$f_\alpha$ ,, ,, ,, O–C–C angular deformation

$f_\beta$ ,, ,, ,, C–O–C ,, ,,

the F and G matrices are given below

**Class** **F** **G**

$$\mathbf{A}_g \begin{bmatrix} f_r & 0 & 0 & 0 \\ 0 & f_d & 0 & 0 \\ 0 & 0 & f_\alpha & 0 \\ 0 & 0 & 0 & f_\beta \end{bmatrix} \begin{bmatrix} \frac{2}{3}\mu_O + \mu_{CH_2} & -\frac{\sqrt{2}}{3}\mu_{CH_2} & \frac{\sqrt{2}}{3}(\mu_O\epsilon - \mu_{CH_2}\tau) & -\frac{4}{3}\mu_O\epsilon \\ -\frac{\sqrt{2}}{3}\mu_{CH_2} & 2\,\mu_{CH_2} & -\frac{4}{3}\mu_{CH_2}\epsilon & \frac{2\sqrt{2}}{3}\epsilon\mu_{CH_2} \\ \frac{\sqrt{2}}{3}(\mu_O\epsilon - \mu_{CH_2}\tau) & -\frac{4}{3}\epsilon\mu_{CH_2} & \frac{11}{6}\mu_O\epsilon^2 + (\epsilon^2 + \tau^2 + \frac{1}{3}\epsilon\tau)\mu_{CH_2} & \\ & & & -\frac{2\sqrt{2}}{3}\mu_O\epsilon^2 \\ & & & -\sqrt{2}\left(\frac{1}{2}\epsilon^2 - \frac{2}{3}\epsilon\tau\right)\mu_{CH_2} \\ -\frac{4}{3}\mu_O\epsilon & \frac{2\sqrt{2}}{3}\epsilon\mu_{CH_2} & -\frac{2\sqrt{2}}{3}\mu_O\epsilon^2 & \\ & & -\sqrt{2}\left(\frac{1}{2}\epsilon^2 - \frac{2}{3}\epsilon\tau\right)\mu_{CH_2} & \frac{8}{3}\mu_O\epsilon^2 + 2\mu_{CH_2}\epsilon^2 \end{bmatrix}$$

$$\mathbf{A}_u \begin{bmatrix} f_r & 0 & 0 \\ 0 & f_\alpha & 0 \\ 0 & 0 & f_\alpha \end{bmatrix} \begin{bmatrix} \frac{4}{3}\mu_O + \mu_{CH_2} & -\frac{\sqrt{2}}{3}\mu_{CH_2} & -\frac{\sqrt{2}}{3}(\mu_O\epsilon + \mu_{CH_2}\tau) \\ -\frac{\sqrt{2}}{3}\mu_{CH_2} & 2\,\mu_{CH_2} & -\frac{4}{3}\epsilon\mu_{CH_2} \\ -\frac{\sqrt{2}}{3}(\mu_O\epsilon + \mu_{CH_2}\tau) & -\frac{4}{3}\epsilon\mu_{CH_2} & \frac{1}{6}\epsilon^2\mu_O + (\epsilon^2 + \tau^2 + \frac{1}{3}\epsilon\tau)\mu_{CH_2} \end{bmatrix}$$

$$\mathbf{B}_g \begin{bmatrix} f_r & 0 \\ 0 & f_\alpha \end{bmatrix} \begin{bmatrix} \frac{4}{3}\mu_O + \mu_{CH_2} & -\sqrt{2}(\frac{1}{3}\epsilon\mu_O + \tau\mu_{CH_2}) \\ -\sqrt{2}(\frac{1}{3}\epsilon\mu_O + \tau\mu_{CH_2}) & \frac{1}{6}\epsilon^2\mu_O + (\epsilon^2 + 3\tau^2 + \epsilon\tau)\mu_{CH_2} \end{bmatrix}$$

$$\mathbf{B}_u \begin{bmatrix} f_r & 0 & 0 \\ 0 & f_\alpha & 0 \\ 0 & 0 & f_\beta \end{bmatrix} \begin{bmatrix} \frac{2}{3}\mu_O + \mu_{CH_2} & \frac{\sqrt{2}}{3}\epsilon\mu_O - \sqrt{2}\mu_{CH_2}\tau & -\frac{4}{3}\mu_O\epsilon \\ \frac{\sqrt{2}}{3}\epsilon\mu_O - \sqrt{2}\tau\mu_{CH_2} & \frac{11}{6}\epsilon^2\mu_O + (\epsilon^2 + 3\tau^2 + \epsilon\tau)\mu_{CH_2} & -\frac{2\sqrt{2}}{3}\epsilon^2\mu_O - \frac{1}{\sqrt{2}}(\epsilon^2 + 2\epsilon\tau)\mu_{CH_2} \\ -\frac{4}{3}\epsilon\mu_O & -\frac{2\sqrt{2}}{3}\epsilon^2\mu_O - \frac{1}{\sqrt{2}}(\epsilon^2 + 2\epsilon\tau)\mu_{CH_2} & \frac{8}{3}\epsilon^2\mu_O + 2\epsilon^2\mu_{CH_2} \end{bmatrix}$$

Using $f_r = 4{\cdot}29 \times 10^5$ dynes/cm. $f_d = 3{\cdot}8 \times 10^5$ dynes/cm.

$f_\alpha = 1{\cdot}365 \times 10^{-11}$ dynes cm./rad. $f_\beta = 0{\cdot}6 \times 10^{-11}$ dynes cm./rad.

the following frequencies were calculated as shown in Table II.

TABLE II

| Class | Calculated | Observed |
|---|---|---|
| $A_g$ (R) | 1100 | 1122 |
| | 827 | 836 |
| | 469 | 433 |
| | 310 | .. |
| $A_u$ (I R) | 1168 | 1136 |
| | 909 | 889 |
| | 268 | .. |
| $B_g$ (R) | 1111 | 1109 |
| | 485 | 482 |
| $B_u$ (I R) | 960 | 1020 |
| | 715 | 740 |
| | 178 | .. |

The observed frequencies in the Raman effect are taken from the measurements of Saksena[3] and those in the infra-red from the measurements of Ramsay.[4] The assignments of Ramsay appear to be wrong because he has not taken the polarisation characters into account. The frequencies 1109 and 482 which are regarded as polarised by Ramsay are actually depolarised in the polarisation measurements of Saksena. Similarly the frequencies 1122 and 433 which have been considered as depolarised by Ramsay are polarised.

The secular equations of dioxane go over to the equations of cyclohexane if we put $\mu_O = \mu_{CH_2}$ and $\epsilon = \tau$. The expressions become identical with those given by Saksena if we put $\cos\phi = -\frac{1}{3}$, $c = \frac{R}{6}$, $a = \frac{\sqrt{2}}{\sqrt{3}}R$ in his expressions. In his paper there is a misprint. In the expression for $\lambda_5^2 + \lambda_6^2$, on page 326 line 7, the expression $(a^2 + c^2)/R^2$ should be $(a^2 + 6c^2)/R^2$.

It is noticed that classes $A_{1g}$, $E_g$ (following the notation of Herzberg[5]) of cyclohexane go to class $A_g$, $A_{1u}$ and $E_u$ to class $A_u$, $A_{2g}$ and $E_g$ to $B_g$ and $A_{2u}$ and $E_u$ to class $B_u$ of dioxane.

### 3. CALCULATION OF RING FREQUENCIES OF TRIOXANE

This molecule is a cyclic trimer of formaldehyde. The crystal structure studies of Moermann[6] show that the molecule exists in a puckered hexagonal or chair structure the C–O bond length being $1{\cdot}42 \pm {\cdot}03$ A and the bond angle of the ring $105° \pm 10°$. The symmetry of the molecule which is shown in Fig. 3 is $C_{3v}$. The axis of the three fold symmetry $C_3^z$ is perpendicular to

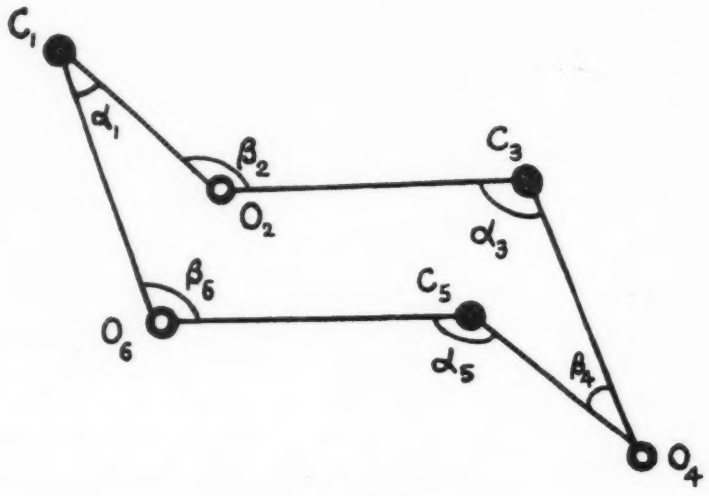


FIG. 3. Trioxane ring.

the planes $O_2O_4O_6$ and $C_1C_3C_5$ and the three planes $3\sigma_v$ are the planes passing through the axis and perpendicular to the above planes and contain two atoms each. The character table for the molecule is given in Table 3.

TABLE III

| $C_{3v}$ | E | $2C_3^z$ | $3\sigma_v$ | $n_i$ | Selection Rule | |
|---|---|---|---|---|---|---|
| | | | | | R | I R |
| $A_1$ | 1 | 1 | 1 | 3 | pol. | *a* |
| $A_2$ | 1 | 1 | −1 | 1 | *f* | *ia* |
| E | 2 | −1 | 0 | 4 | dep. | *a* |

The internal symmetry co-ordinates are:—

Class $A_1$ $$R_1 = \frac{1}{\sqrt{6}}(r_{12} + r_{23} + r_{34} + r_{45} + r_{56} + r_{61})$$

$$R_2 = \frac{1}{\sqrt{3}}(\alpha_1 + \alpha_3 + \alpha_5)$$

$$R_3 = \frac{1}{\sqrt{3}}(\beta_2 + \beta_4 + \beta_6)$$

Class $A_2$ $$R_1 = \frac{1}{\sqrt{6}}(r_{12} - r_{23} + r_{34} - r_{45} + r_{56} - r_{61})$$

Class E $$R_{1a} = \frac{1}{\sqrt{12}}[2(r_{23} + r_{56}) - (r_{45} + r_{12}) - (r_{61} + r_{34})]$$

$$R_{1b} = \tfrac{1}{2}[(r_{45} + r_{12}) - (r_{61} + r_{34})]$$

$$R_{2a} = \tfrac{1}{2}[-(r_{45} - r_{12}) + (r_{61} - r_{34})]$$

$$R_{2b} = \frac{1}{\sqrt{12}}[2(r_{23} - r_{56}) - (r_{45} - r_{12}) - (r_{61} - r_{34})]$$

$$R_{3a} = \frac{1}{\sqrt{12}}[2(\alpha_1 + \beta_4) - (\alpha_3 + \beta_6) - (\alpha_5 + \beta_2)]$$

$$R_{3b} = \tfrac{1}{2}[(\alpha_3 + \beta_6) - (\alpha_5 + \beta_2)]$$

$$R_{4a} = \frac{1}{\sqrt{12}}[2(\alpha_1 - \beta_4) - (\alpha_3 - \beta_6) - (\alpha_5 - \beta_2)]$$

$$R_{4b} = \tfrac{1}{2}[(\alpha_3 - \beta_6) - (\alpha_5 - \beta_2)]$$

If $f_r$ is the force constant for C-O valence

$f_\alpha$ „ „ O–C–O deformation

$f_\beta$ „ „ C–O–C „

$\epsilon$ is the reciprocal of C–O bond length, and all the bond angles are 109° 28′.

The F and G matrices are given below:—

Class

$$A_1 \begin{bmatrix} f_r & 0 & 0 \\ 0 & f_\alpha & 0 \\ 0 & 0 & f_\beta \end{bmatrix} \begin{bmatrix} \frac{2}{3}(\mu_O + \mu_{CH_2}) & \frac{2}{3}(\mu_O - 2\mu_{CH_2})\epsilon & \frac{2}{3}(\mu_{CH_2} - 2\mu_O)\epsilon \\ \frac{2}{3}(\mu_O - 2\mu_{CH_2})\epsilon & \left(\frac{11}{3}\mu_O + \frac{8}{3}\mu_{CH_2}\right)\epsilon^2 & -\frac{4}{3}(\mu_O + \mu_{CH_2})\epsilon^2 \\ \frac{2}{3}(\mu_{CH_2} - 2\mu_O)\epsilon & -\frac{4}{3}(\mu_O + \mu_{CH_2})\epsilon^2 & \frac{1}{3}(8\mu_O + 11\mu_{CH_2})\epsilon^2 \end{bmatrix}$$

$$A_2 \quad [f_r] \qquad \left[\frac{4}{3}(\mu_O + \mu_{CH_2}\right]$$

Class

$$E\begin{bmatrix} f_r & 0 & 0 & 0 \\ 0 & f_r & 0 & 0 \\ 0 & 0 & \frac{1}{2}(f_\alpha+f_\beta) & \frac{1}{2}(f_\alpha-f_\beta) \\ 0 & 0 & \frac{1}{2}(f_\alpha-f_\beta) & \frac{1}{2}(f_\alpha+f_\beta) \end{bmatrix}$$

$$\begin{bmatrix} \frac{7}{6}(\mu_O+\mu_{CH_2}) & \frac{1}{\sqrt{12}}(\mu_{CH_2}-\mu_O) & \frac{2\sqrt{2}}{3}(\mu_{CH_2}+\mu_O)\epsilon & 0 \\ \frac{1}{\sqrt{12}}(\mu_{CH_2}-\mu_O) & \frac{5}{6}(\mu_O+\mu_{CH_2}) & \frac{\sqrt{2}}{\sqrt{3}}(\mu_O-\mu_{CH_2})\epsilon & -\frac{2}{\sqrt{6}}(\mu_{CH_2}+\mu_O)\epsilon \\ \frac{2\sqrt{2}}{3}(\mu_{CH_2}+\mu_O)\epsilon & \frac{\sqrt{2}}{\sqrt{3}}(\mu_O-\mu_{CH_2})\epsilon & \frac{31}{12}(\mu_{CH_2}+\mu_O)\epsilon^2 & \frac{3}{4}(\mu_{CH_2}-\mu_O)\epsilon^2 \\ 0 & -\frac{2}{\sqrt{6}}(\mu_{CH_2}+\mu_O)\epsilon & \frac{3}{4}(\mu_{CH_2}-\mu_O)\epsilon^2 & \frac{5}{4}(\mu_{CH_2}+\mu_O)\epsilon^2 \end{bmatrix}$$

The above expressions for the ring frequencies of trioxane go over into the expressions for the ring frequencies of cyclohexane if we put

$$\mu_O = \mu_{CH_2}, \text{ and } f_\alpha = f_\beta.$$

TABLE IV

| | Trioxane | | Cyclohexane | Dioxane |
|---|---|---|---|---|
| Class | Calculated | Observed | Observed | Observed |
| $A_1$ | 941 | 930 (R) ?<br>937 (I.R.) | 802 ($A_{1g}$) | 836 ($A_g$) |
| | 747 | 747 (R) | 719 ($A_{2u}$) | 740 ($B_u$) |
| | 373 | .. | 382 ($A_{1g}$) | .. |
| $A_2$ | 1142 | .. | 1110 ($A_{1u}$)* | 1136 ($A_u$) |
| E | 1144 | 1164 (I.R.) | 1028 ($E_g$) | 1109 ($B_g$)<br>1122 ($A_g$) |
| | 979 | 958 (R)<br>972 (I.R.) | 903 ($E_u$) | 889 ($A_u$)<br>1020 ($B_u$) |
| | 484 | 520 (R) | 426 ($E_g$) | 433 ($A_g$)<br>482 ($B_g$) |
| | 189 | 219 (R) ? | .. | .. |

* Observed by Ramsay[7] in the infra-red with intensity zero in the liquid state.

The classes $E_g$ and $E_u$ of cyclohexane go to class E, the classes $A_{1g}$ and $A_{2u}$ to class $A_1$, and the class $A_{1u}$ to class $A_2$ of trioxane.

Taking the C–O bond length as 1·42 Å and using the C–O force constant $(f_r) = 4{\cdot}3 \times 10^5$ dynes/cm and the O–C–O deformation $(f_\alpha)$ $2{\cdot}0 \times 10^{-11}$ dynes cm./rad. and the C–O–C deformation $(f_\beta)$ as $\cdot 6 \times 10^{-11}$ dynes. cm/rad., we have calculated the ring frequencies of trioxane in Table IV. Observed ring frequencies in cyclohexane and dioxane are also given for comparison.

The Raman frequencies are from the measurements of Kahovec and Kohlrausch[8] made in solution in $CCl_4$ and infra-red frequencies are from the measurements of Ramsay[9] also made in solution in $CCl_4$. Polarisation measurements have not been made and so it is not possible to assign all the frequencies properly. However the assignments given above appear to be quite probable and almost agree with the assignments of Ramsay except for the frequency 958 which he takes in Class $A_1$.

## Summary

Wilson's F and G matrix method has been used to obtain expressions for the ring frequencies of dioxane and trioxane. The C–O and C–C force constants have been found to be 4·3 and $3{\cdot}8 \times 10^5$ dynes/cm. and the O–C–O and O–C–C deformation force constants as 2·0 and $1{\cdot}4 \times 10^{-11}$ dynes. cm/rad. respectively and C–O–C force constants as $0{\cdot}6 \times 10^{-11}$ dynes cm./rad.

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# STUDIES ON NIOBIUM AND TANTALUM

## Part V. Tartratotantalates

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### Introduction

Tantalum is always associated with niobium in its natural occurrence and bears a very close resemblance to niobium in many of its chemical properties. Tantalum has come to prominence recently and has found many industrial applications (Balke, 1948, 1938, 1935). It is now classified as a strategic material. Though investigations on its compounds are not very extensive, some tantalates of the alkali metals have been prepared and studied principally by Rose (1857), Balke and Smith (1908), Jander and Schultz and Windmaisser (1941).

Very little attention seems to have been bestowed on the complex compounds of tantalum with oxalic and tartaric acids; the only one well-defined complex compound isolated so far is the potassium oxalo-tantalate $5\,K_2O \cdot Ta_2O_5 \cdot 10\,C_2O_3$, by Russ (1902). No tartrato complex of tantalum is known. Since a well-defined series of salts called tartratoniobates was formed in the case of niobium (this author, 1950), the possibility of the existence of a similar class of compounds of tantalum with tartaric acid was investigated in view of the close resemblance of tantalum to niobium.

### Experimental

*Preparation and Purity of* $Ta_2O_5$.—Tantalum pentoxide was prepared by decomposing pure white flakes of Kahlbaum's potassium tantalum fluoride with concentrated sulphuric acid, treating with water, collecting the precipitated tantalic acid, washing and igniting it to the pentoxide. The tantalum pentoxide was ignited with ammonium carbonate at 800° C. in the muffle furnace; the pentoxide obtained was a bright white powder with a brilliant lustre. It was analysed and found to contain silica in traces; iron, heavy metals and niobium were absent; $TiO_2$ was present to the extent of 0·2%. Therefore the purity of the sample of $Ta_2O_5$ is 99·8%.

*Potassium* (4 : 3) *tantalate*.—Tantalum pentoxide (10 g.) and potassium carbonate (15 g.) were intimately mixed and heated in a platinum dish for

6 hours at 850° C. The melt was taken up in hot water and an insoluble residue (1 g.) of pentoxide removed. The clear filtrate was concentrated to crystallisation; the crystals obtained were filtered under suction, washed with ice-cold water, dried and analysed as follows:

A weighed quantity of the tantalate was dissolved in water and tantalic acid precipitated by the addition of hydrochloric acid; it was filtered, washed, ignited and weighed as $Ta_2O_5$. From the filtrate the alkali metal was determined as the chloride by the customary method. $H_2O$ was determined by difference. The results obtained with potassium tantalate are enumerated in Table I.

TABLE I

| | Found % | Calculated for $4\,K_2O \cdot 3\,Ta_2O_5 \cdot 16\,H_2O$ % |
|---|---|---|
| $K_2O$ .. .. | 19·05 | 18·93 |
| $Ta_2O_5$ .. .. | 66·71 | 66·58 |
| $H_2O$ .. .. | 14·24 | 14·49 |

Therefore the potassium tantalate prepared has the composition $4\,K_2O \cdot 3\,Ta_2O_5 \cdot 16\,H_2O$.

*Sodium* (4: 3) *tantalate.*—Tantalum pentoxide (2 g.) was fused with sodium carbonate (3 g.) at 850° C. for 5 hours. The melt was washed with cold water to remove the excess of the alkali carbonate. The residue was extracted twice with hot water and the extract concentrated to crystallisation. The crystals were filtered, washed, dried and analysed. It gave the following results:

TABLE II

| | Found % | Calculated for $4\,Na_2O \cdot 3\,Ta_2O_5 \cdot 25\,H_2O$ % |
|---|---|---|
| $Na_2O$ .. .. | 12·32 | 12·26 |
| $Ta_2O_5$ .. .. | 65·70 | 65·50 |
| $H_2O$ .. .. | 21·98 | 22·24 |

Therefore the compound prepared agrees to the formula $4\,Na_2O \cdot 3\,Ta_2O_5 \cdot 25\,H_2O$. Sodium (4: 3) tantalate was also prepared as a microcrystalline

powder by adding a concentrated solution of sodium chloride to the solution of potassium (4 : 3) tantalate.

*Alkali tartrato-tantalate.*—It became evident through preliminary trials that a complex compound was formed between tantalum and *d*-tartaric acid. The reaction was carried out by treating alkali tantalates with tartaric acid, isolating the products of reaction and analysing them. A class of compounds called the tartrato-tantalates has been prepared; they are analogous to the tartratoniobates in their properties and behaviour. The sodium and potassium salts were prepared as outlined below.

2-*Potassium*-2-*tartrato*-2-*tantalate.*—Potassium (4 : 3), tantalate (6 g.) was dissolved in water and treated with tartaric acid (5 g.). The clear solution was cooled in ice for one hour and a white precipitate of potassium hydrogen tartrate that was formed was removed. The filtrate was concentrated on the water-bath when the solution became viscous and jelly-like as met with in the case of the tartratoniobates, without any separation of crystals. Other attempts at crystallisation failed; therefore resort was taken to the addition of alcohol when a white substance was thrown down. It was filtered under gentle suction, washed with alcohol and dried (8·8 g.). It was analysed by precipitating tantalic acid from its solution with hydrochloric acid, collecting the precipitate, igniting and weighing it as $Ta_2O_5$. From the filtrate, the alkali was estimated as KCl. Tartaric acid was determined in the sample by potassium iodate method. $H_2O$ was computed by difference. It gave the following results:

TABLE III

| | Found % | Calculated for $K_2O \cdot Ta_2O_5 \cdot (C_4H_4O_5)_2 \cdot 9\,H_2O$ % |
|---|---|---|
| $K_2O$ .. .. | 9·92 | 9·79 |
| $Ta_2O_5$ .. .. | 45·65 | 45·92 |
| $C_4H_4O_5$ .. .. | 27·82 | 27·44 |
| $H_2O$ .. .. | 16·61 | 16·85 |

Therefore the compound formed has the composition

$K_2O \cdot Ta_2O_5 \cdot (C_4H_4O_5)_2 \cdot 9\,H_2O$, and can be named as 2-potassium-2-tartrato-2-tantalate 9-hydrate.

2-*Sodium*-2-*tartrato*-2-*tantalate.*—This was similarly prepared by reacting sodium (4 : 3) tantalate (3·5 g.) with tartaric acid (3 g.). The first

crop obtained was found to be sodium hydrogen tartrate. The final solution remained viscous and the substance was separated with the addition of alcohol. A white substance was got (4·6 g.) which was also analysed by the abovementioned method with the following results:

TABLE IV

| | Found % | Calculated for $Na_2O \cdot Ta_2O_5 \cdot (C_4H_4O_5)_2 \cdot 8\ H_2O$ % |
|---|---|---|
| $Na_2O$ .. .. | 6·91 | 6·8 |
| $Ta_2O_5$ .. .. | 48·32 | 48·46 |
| $C_4H_4O_5$ .. .. | 29·25 | 28·95 |
| $H_2O$ .. .. | 15·52 | 15·79 |

Hence the compound corresponds to the formula

$Na_2O \cdot Ta_2O_5 \cdot (C_4H_4O_5)_2 \cdot 8\ H_2O$, and it is named as 2-sodium-2-tartrato-2-tantalate 8-hydrate.

*Properties.*—The sodium and potassium tartratotantalates are white powdery substances, freely soluble in water. Their aqueous solutions are stable in air unlike the tantalates which undergo quick decomposition. On treatment with mineral acids, tantalic acid is thrown down as a flocculent white precipitate. The solutions give a yellow coloration with tannin and a fine thick yellow precipitate with the addition of a mineral acid. They are acid salts and are acidic to methyl orange. They give a red coloration to a solution of ammonium vanadate. They are decomposed by alkali hydroxides. In general the tartratotantalates resemble the tartratoniobates in many of their properties.

## DISCUSSION

It has been seen that the alkali tantalates by reaction with tartaric acid yield tartrato-complexes of the type 2-tartrato-tantalate. It could be expected that tantalum, in view of its close resemblance to niobium in its chemical properties, would give tartratotantalates similar to the tartratoniobates which have been studied in detail. The higher order tartrato-compounds of tantalum are extremely difficult to crystallise from aqueous solutions and the use of alcohol has been resorted to for aiding crystallisation. The tartratotantalates are obtained as acidic salts and they answer the characteristic reactions of heteropoly acids.

The formation of the 2-tartrato-2-tantalate of the alkali metals can be explained on the basis that the stable alkali tantalate in solution is the alkali (1 : 1) tantalate and all other tantalates are hydrolysed in solution yielding the alkali (1 : 1) tantalate and free alkali hydroxide according to the following equations:

$$4\,K_2O.3\,Ta_2O_5.aq \rightarrow 3\,(K_2O.Ta_2O_5.aq) + 2\,KOH$$

$$4\,Na_2O.3\,Ta_2O_5.aq \rightarrow 3\,(Na_2O.Ta_2O_5.aq) + 2\,NaOH.$$

The alkali (1 : 1) tantalate by reaction with tartaric acid yields the 2-tartrato-2–tantalate while the free alkali hydroxide forms the alkali tartrate. The reaction can be represented by the following equations:

$$4\,K_2O.3\,Ta_2O_5.aq + 8\,C_4H_6O_6 \rightarrow 3\,[K_2O.Ta_2O_5.(C_4H_4O_5)_2.aq] + 2\,KHC_4H_4O_6.$$

$$4\,Na_2O.3\,Ta_2O_5.aq + 8\,C_4H_6O_6 \rightarrow 3\,[Na_2O.Ta_2O_5.(C_4H_4O_5)_2.aq] + 2\,NaHC_4H_4O_6.$$

The formation of the 2-tartrato-2-tantalate can be explained in terms of the Miolati-Rosenheim theory of the heteropoly acids. According to this theory tantalum is always hydrated and attached to 6 atoms of oxygen. Thus the parent tantalate in solution is the alkali (1 : 1) tantalate $M\,TaO_3.3\,H_2O$ or $M\,H_6\,(TaO_6)$ where M = Na or K. Replacement of oxygen atoms takes place by one tartrate radical with the consequence that the tartratotantalate $R\,H_4\left[\begin{matrix}O_4\\Ta\\(C_4H_4O_6)\end{matrix}\right]$ aq. is formed. A more saturated compound is not found from the experiments and this behaviour is similar to that of niobium. The alkali tartratotantalates that have been prepared can be represented by the following structure:

$$M\,H_4\left[\begin{matrix}O_4\\Ta\\(C_4H_4O_6)\end{matrix}\right] n\,H_2O\,,$$

where M = Na or K and $n = a$ varying number. Thus it can be seen that a class of compounds called the 2-tartrato-2-tantalates has been prepared and that it can be represented by heteropoly acid structure shown above.

## SUMMARY

It has been shown that literature does not reveal the existence of any complex compound of tantalum with tartaric acid. Experiments conducted

yielded tartratocomplexes with sodium and potassium tantalates. The complexes have been analysed and their properties found to be similar to those of the tartratoniobates. The mode of formation of these compounds has been explained. They are formulated with heteropoly acid structures of the general type

$$M\,H_4\left[\begin{array}{c} O_4 \\ Ta \\ (C_4H_4O_6) \end{array}\right] n\,H_2O$$

where M = Na or K and n = a varying number.

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# CHEMICAL EXAMINATION OF THE FATTY OIL FROM THE SEEDS OF *STECULIA URENS* ROXB.

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Hilditch, *et al.*, in their investigation[1] on the fatty oil from the seeds of *Sterculia fœtida* Roxb. have reported that the oil contains over 70% of a branched chain polyethenoid acid of $C_{19}$ series. The observation is rather unusual in that a branched chain fatty acid has been found in nature as a major component of a seed fat and that too it is reported to consist of an odd number of carbon atoms. In this connection it has been also reported by Hilditch (*loc. cit.*) that the seed fats of *S. fœtida*, *S. platonifolia* and *Theobroma cacao* (fam. Sterculaceæ) show great diversity in composition in contrast to the general rule of similarity in component acids between seed fats from the same botanical family. It was, therefore, thought worthwhile to investigate the component fatty acids of the oil from the seed kernels of the indigenous Sterculia species, *Sterculia urens* Roxb. particularly to see if like *S. fœtida*, it also yields a large quantity of a polyethenoid acid and proves to be a valuable paint oil, if not at least a good edible or a soap stock oil.

2. *Sterculia urens* is a large deciduous gregarious tree[2] commonly found in the dry forests of Northern India throughout Central India and the Deccan and on the West Coast in the Konkan and Kanara. The gum which exudes from the tree or which is tapped from it is known as gum Karaya or gum Katira and is already a well known commercial article and a good dollar earner, being used as a substitute for gum tragacanth. The seeds are said to be roasted and eaten by the aboriginal tribes of Madhya Pradesh.

Samples of *Sterculia urens* air dry seeds received through the courtesy of the Forest Departments of Vindhya Pradesh, Madhya Pradesh, Madhya Bharat and Bombay consisted of 43·3% peri-carp and 56·7% kernel. The latter yielded 25% of a light yellow non-drying oil, both by petroleum ether and ethyl ether extraction. The petroleum ether extracted oil was lighter in colour, but otherwise there was hardly any difference in the physical and chemical properties of the two oils.

TABLE I

*Chemical and Physical Constants of the Fatty Oil*

| | |
|---|---|
| Specific gravity at 30° C. | 0·9143 |
| Refractive index at 30° C. | 1·4587 |
| Optical rotation | Nil |
| Acid value | 1·8 |
| Saponification value | 195·8 |
| Ester value | 194·0 |
| Iodine value | 74·2 |
| Acetyl value | 45·0 |
| Hehner value | 91·4 |
| Unsaponifiable matter | 0·55% |

The usual technique as described in the previous papers[3] from this laboratory for the preparation of the mixed fatty acids, removal of the unsaponifiable matter from them, their separation mainly into "solid" and "liquid" acids by Twitchell's[4] modified lead salt-alcohol method[5] has been followed. The "solid" and "liquid" acids were also worked up in the usual manner to isolate and identify the constituent acids. The following data has been recorded:—

TABLE II

*Chemical and Physical Constants of the mixed Fatty Acids*

| | |
|---|---|
| Neutralisation value | 198·47 |
| Mean molecular weight | 282·1 |
| Iodine value | 77·4 |
| Softening point | 34·5° C. |
| Melting point | 38·5° C. |

TABLE III

*Separation of the Mixed Acids by Twitchell's Method*

| Acids | | Iodine value |
|---|---|---|
| (S) Solid | 23·3% | 6·4 |
| (S) Semi-solid | 4·0% | 29·8 |
| (L) Liquid | 67·7% | 94·0 |
| (R) Resin | 4·95% | .. |

## SOLID ACIDS

The solid fatty acids (62 g.) were converted into their methyl esters in the usual manner with 3% methyl alcoholic hydrochloric acid. The methyl ester (55 g.) thus obtained was fractionated under reduced pressure (5 mm. of mercury) in Claisson flask as follows:—

TABLE IV

| Fraction | B.P. | Weight of ester fraction | Iodine value | Weight of fatty acids | Mean Mol. wt. of fatty acids |
|---|---|---|---|---|---|
| S1 .. | 154° C–174° C | 3·16 g. | 2·23 | 4·48 g. | 244·8 |
| S2 .. | 174° C–179° C | 3·30 g. | 2·25 | | |
| S3 .. | 179° C–182° C | 18·65 g. | 2·72 | 16·90 g. | 290·2 |
| S4 .. | 183° C–187° C | 11·80 g. | 4·38 | 10·39 g. | 250·8 |
| S5 .. | 188° C–192° C | 4·80 g. | 6·87 | 6·59 g. | 289·1 |
| S6 .. | 193° C–199° C | 3·87 g. | 10·75 | | |
| | | | | 38·36 g. | |
| Residue .. | | 6·17 g. | 38·7 | 5·45 g. | |
| | | | | 43·81 g. | |
| Loss .. | | 3·25 g. | .. | .. | |

All these fractions were saponified separately and the corresponding acids liberated by hydrochloric acid. Each of the acid fraction was fractionally chrystallized from dilute acetone and subsequently from benzene to isolate the individual acids. These have been identified as myristic, palmitic, stearic and lignoceric acids by their neutral equivalent and mixed melting points with authentic samples.

Calculating from the above data the composition of the solid acids turns out to be as follows:—

| | |
|---|---|
| Myristic acid .. .. .. .. | 17·85% |
| Palmitic acid .. .. .. .. | 68·49% |
| Stearic acid .. .. .. .. | 7·71% |
| Lignoceric acid .. .. .. .. | 6·04% |
| | 100·00% |

## LIQUID ACIDS

3·2836 g. of the liquid fatty acids were dissolved in 60 c.c. of dry ether and brominated according to the method of Lewkowitch.[6] No hexa bromides separated out, which indicated the absence of linolenic acid.

The ethereal solution was washed free of excess of bromine by aqueous solution of sodium thiosulphate, washed with water, dried with anhydrous

magnesium sulphate, filtered into a weighed flask and the ether distilled off. The yield of the brominated product was 5·2147 g. (Bromine by Carius' method 37·01%).

The mixed crude bromides were dissolved in petrolium ether and cooled in a refrigerator to crystallise linoleic acid tetra-bromide. The pure crystals were filtered and recrystallised from petroleum ether (m.p.= 114° C.) Calculating from the above data the composition of the liquid acids found to be as follows:—

| | |
|---|---|
| Oleic acid .. .. .. .. .. | 96·5% |
| Linoleic acid .. .. .. .. | 3·5% |

Based on the above results for solid and liquid acids the composition of the mixed acids works out as follows:—

| Acid | |
|---|---|
| Myristic (Saturated acids lower than palmitic) .. | 4·65% |
| Palmitic .. .. .. .. .. | 17·82% |
| Stearic .. .. .. .. .. | 2·01% |
| Lignoceric .. .. .. .. .. | 1·57% |
| Oleic .. .. .. .. .. | 66·59% |
| Linoleic .. .. .. .. .. | 2·42% |
| Resin .. .. .. .. .. | 4·95% |

## Unsaponifiable Matter

The unsaponifiable matter, obtained from the sodium soaps of the mixed acids by extraction with ethyl ether when crystallised from alcohol (95%) melted at 123° C. On recrystallisation twice from the same solvent crystals melting at 129° C., $[\alpha]_D^{28}$—77·4° (C = 0·4520% in carbon tetrachloride) were obtained. The acetyl derivative of the product melted at 121° C., $[\alpha]_D^{28}$— 38·0° (C = 0·7688% in carbon tetrachloride). The product appears to be sitosterol, the common phytosterol found in seed fats.

## Discussion and Conclusion

The major component acids of the fatty oil have been found to consist of oleic and palmitic acids and the minor ones of linoleic, lignoceric, stearic and saturated acids lower than palmitic. This distribution does not agree with the components of the fatty oils[7] of other *Sterculiaceæ* genera and species so far analysed, namely *S. fœtida*, *S. parviflora*, *S. platonifolia*, *S. tomentosa*, *Brachychiton deversifolium* and *Theobroma cacao*. This supports the finding of *Hilditch*[8] that " Sterculiaceæ is one of the comparatively few botanical families in which seed fats of different genera and even species are

markedly dissimilar in their component acids". One of the objects of this investigation was to see if the fatty oil from *S. urens* seeds contained the polyethenoid acid similar to that reported in the oil of *S. fœtida*. This has, however, not been found to be the case.

The fatty oil belongs to the non-drying class and could be either used for edible purposes or for soap making.

## SUMMARY

1. The chemical and physical constants of the fatty oil, its component fatty acids and its Sterol from the unsaponifiable matter are described.

2. The oil has been found to consist of the glycerides of palmitic, stearic, lignoceric, oleic and linoleic acids besides small qualities of resin acids and of glycerides of acids lower than palmitic.

3. The unsaponifiable matter yielded sitosterol, the common phytosterol found in seed fats.

4. The oil did not contain any polyethenoid acid similar to that reported in the fatty oil from the seeds of *S. fœtida* by Hilditch.

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# LIFE-TIME OF $\mu$-MESONS

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The disintegration curves of positive $\mu$-mesons at rest in two absorbers lead and paraffin, have been determined experimentally by an oscilloscopic method using cosmic ray mesons at sea level as the source of $\mu$-mesons. In this paper a detailed description of the electronic apparatus constructed for this purpose as also the results of the measurement of the mean life-time of positive mesons in the two absorbers is given.

## Experimental

The method for the determination of the life-time is similar to that of Ticho (1947). A cross sectional view of the counter geometry used and a block diagram of the principal circuits are given in Fig. 1. The electron

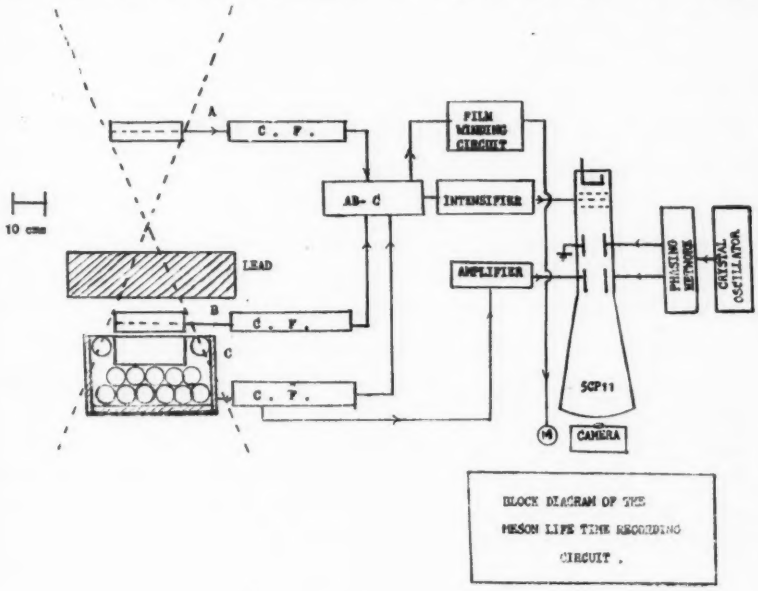


Fig. 1

beam of an oscilloscope is made to describe a circle with a frequency of 100 kilo cycles per second. The bias on the grid of the cathode ray tube is adjusted so that normally there is no visible trace of the circle on the screen. A meson passing through the counters A and B (Fig. 1) and stopping in the absorber gives an anticoincidence pulse AB–C which after amplification triggers an intensifier gate of 15 microseconds width. This square topped pulse brightens the beam and a blue circle is traced on the screen. If the meson that stops decays into an electron, and the electron discharges one of the counters in the tray C, then this pulse from C deflects the beam away from its circular path and instead of a complete circle only an arc of a circle is traced and the arc length is proportional to the life-time of the meson that decays. In either case the trace is photographed and the film is advanced through the required length by the film winding circuit.

The trays A and B consisted of 4 Geiger counters of length 15 cm. and diameter 4·5 cm. Three slabs of lead (50 cm. × 50 cm.) each 3·5 cm. thick were placed between the trays A and B. The counter tray C consisted of 13 counters of length 30 cm. and diameter 4·5 cm. All the counters were filled at a pressure of 10 cm. with Argon and petroleum-ether in the ratio of 9 : 1.

Typical oscilloscopic records of the decay events registered are reproduced in Fig. 2.

The electronic equipment comprises of the following units (Fig. 3):

1. Coincidence anti-coincidence circuits.
2. Circular sweep pulse timing circuit.
3. Micro-second delay double pulse generator.
4. Film winding circuit.
5. Decimal scaler.
6. Stabilized low voltage and high voltage supplies.

The coincidence, anti-coincidence circuits are of the usual Rossi type, the acorn pentodes 954 which have low inter electrode capacitance having been used as the coincidence and anti-coincidence tubes. The negative pulse from the anti-coincidence plate is inverted and fed to the grid of the thyratron 884. A telephone call counter in the plate circuit of the thyratron records the number of anti-coincidence pulses.

The sweep circuit consists of a 100 k.c.s. crystal controlled sine wave oscillator followed by an R.F. amplifier and a phasing net work. For the oscillator, half of a 6 SN 7 double triode is used and the amplifier is a 6 SJ 7

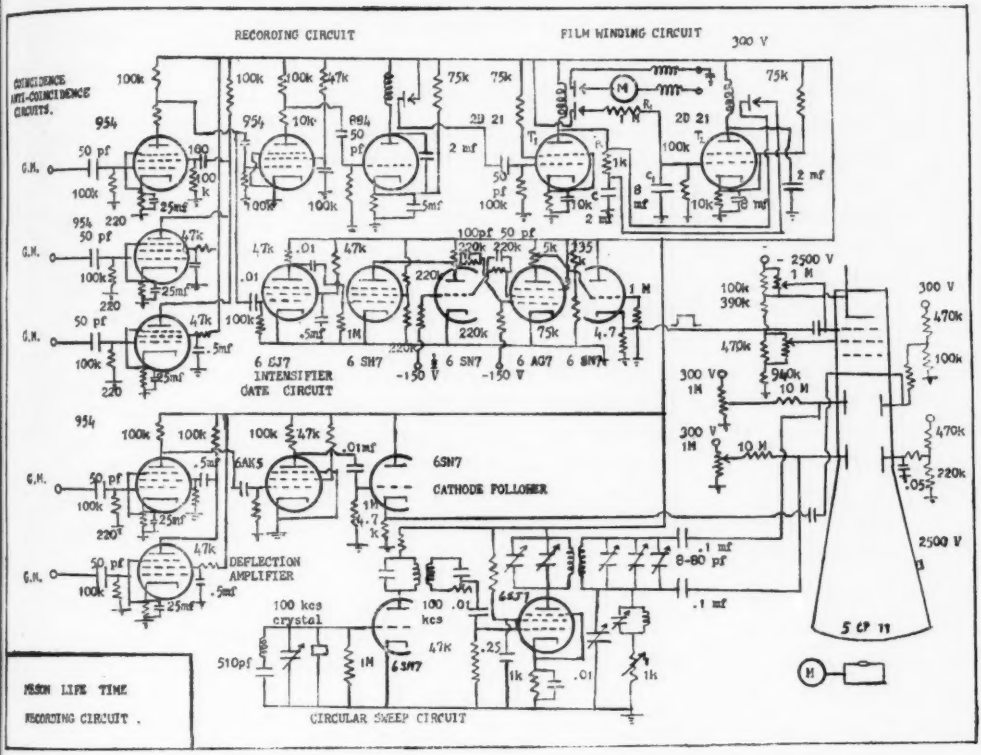


FIG. 3

tube with a transformer in the plate circuit tuned to 100 k.c.s. The phasing net work is of the RC type and is similar to that described by Ticho (1947).

The intensifier circuit comprises of a flip-flop, one half of which is half of a 6 SN 7 triode and for the other half the cathode, grid and the screen electrodes of a 6 AG 7 pentode are used. When the circuit is triggered the fast positive gate developed at the plate electrode is used to brighten the trace on the oscilloscope screen. The gate width is adjusted to be 15 micro seconds and is fed to the scope through a cathode follower.

The deflection amplifier consists of three stages of pentode amplifiers, followed by a cathode follower. The final pulse has a very sharp rise time and the amplitude of the pulse is sufficiently large to throw the beam completely out of the screen.

The 5 CP 11 blue screen tube is used for the oscilloscope with an overall voltage of 5,000 volts between the cathode and the post deflection accelerator. Photographs are taken on Plus X film with f/1·5 coated lens of a Contax camera, and developed with Kodak D 76 developer.

The film winding circuit works as follows: The thyratron $T_1$ (Fig. 3) fires whenever a positive pulse is fed to its grid. It is not immediately switched off because of the large resistance in series with the quenching condenser C. The relay connected in the plate circuit of the thyratron puts on the film winding motor. Another pair of contacts of the same relay are used to charge the condenser $C_1$ through the resistance $R_1$. The condenser $C_1$ is connected in the grid circuit of a second thyratron $T_2$. As soon as the voltage on the condenser rises above the bias voltage, the thyratron fires, but is immediately switched off by the condenser $C_2$. The relay in the plate circuit of $T_2$ is used to short the resistance R in series with the condenser C, thus switching off the thyratron $T_1$ and consequently the motor. The time after which $T_1$ is switched off naturally depends on the time constant $R_1C_1$, and the bias on $T_2$. The time for which the motor has to be on is determined by the amount of film to be advanced and can be controlled by the potentiometer $R_1$.

A motor with a reduction gear with a final speed of $\frac{1}{3}$ revolution per second was used to wind the film. The positive pulse to the first thyratron was given by the coming on of the relay in the plate of thyratron in the recording circuit.

To test the performance of the pulse-timing circuit, periodically, a microsecond delay double pulse generator was built. The pulse generator consists of a self-oscillating thyratron followed by cathode follower shaping circuits. A delayed output is obtained by passing the pulse from the thyratron through a delay univibrator and shaping circuits. The delay can be adjusted to be 1, 5 and 10 microseconds, by varying the time constants of the univibrator by a band switch. A fine control of the delay is possible by varying the amplitude of the pulse from the plate of the thyratron.

In order to obtain the plateaux of Geiger counters and also for recording the counting rates of the trays, a decimal scaler was constructed. It comprises of two scales of ten in series, each of which is a ring of five and a binary scale of two. The twin triodes 6 SN 7 have been used for all the Eccles-Jordan trigger pairs of the scaling stages. An input amplifier and a discriminator precede the first scale of ten. A Londex half hour dial timer has been provided to start the scaling stage when desired and stop it after a known interval of time.

The stabilised low voltage and high voltage supplies are of the usual type.

## Experimental Results

Two series of experiments were carried out. In the first positive and negative mesons were not separated and the experimental arrangement used is shown in Fig. 1. The absorber used was lead. Since the absorption probability varies as $Z^4$, the chance for the decay of negative mesons in absorbers like lead ($Z = 82$) is extremely small compared to absorption. Therefore the disintegration curve obtained in the case of lead can be considered as arising due to the decay of positive mesons only. The disintegration curve for lead is presented in Fig. 4. The ordinate is plotted in the

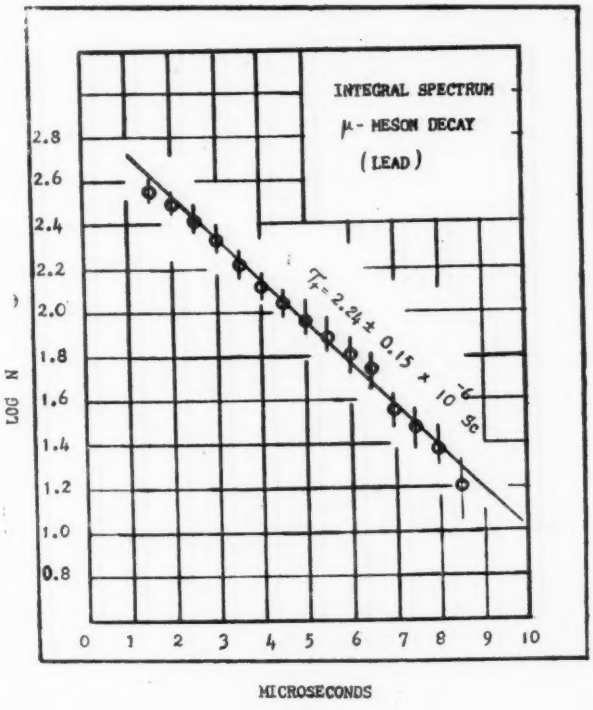


Fig. 4

logarithmic scale and represents the number of mesons that decayed with a life-time greater than the corresponding abscissa represented in microseconds. The points are fitted to a line by the method of least squares. The mean life-time determined from the slope of the line comes out as $2{\cdot}24 \pm 0{\cdot}17$

microseconds. A more elaborate statistical analysis of the results gives a value $\tau_+ = 2 \cdot 193$ microseconds (see Appendix). Very few decay events were registered in the interval 0 to 1 microsecond. This was because the anti-coincidence tray itself was used for the detection of the delayed electrons and the anti-coincidence circuit had a resolving time of about one microsecond. The slightly lower values (Fig. 4) for the first two intervals can also be attributed to the same reason. Therefore for the statistical analysis, data corresponding to the period greater than 2·5 microseconds were taken into consideration.

In the second experiment, positive and negative mesons were separated by a magnetic lens similar in construction to that described by Bernardini, *et al.* (1945). The counter geometry employed is shown in Fig. 5. Positive

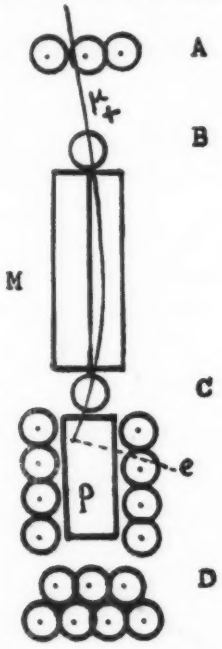


FIG. 5. Experimental Arrangement II
Positive mesons focussed into the paraffin absorber in which they decay, by the magnetic lens M.

mesons with energy between 250 Mev and 300 Mev were concentrated into the paraffin absorber by the magnetic lens M. The field inside the iron which was adjusted to be 5,000 gauss was sufficient to deflect the negative

mesons in the same energy range completely out of the paraffin absorber. A simple consideration of the action of the magnetic lens shows that for the decay experiment a comparatively low magnetic field of the order of 2,500 to 5,000 gauss is more efficient in separating positives from negatives than a higher field. The anti-coincidence ABC–D was used to intensify the beam and the delayed pulse from tray D to deflect the beam away from its circular path. The counters A, B and C were 30 cm. in length and 4·5 cm. in diameter. The counters in tray D were 37·5 cm. in length and 4·0 cm. in diameter. On the average about 4 decays were recorded for ten hours operation every day.

The integral spectrum obtained in the case of paraffin for positive mesons is given in Fig. 6. The mean life-time determined from the slope of the line

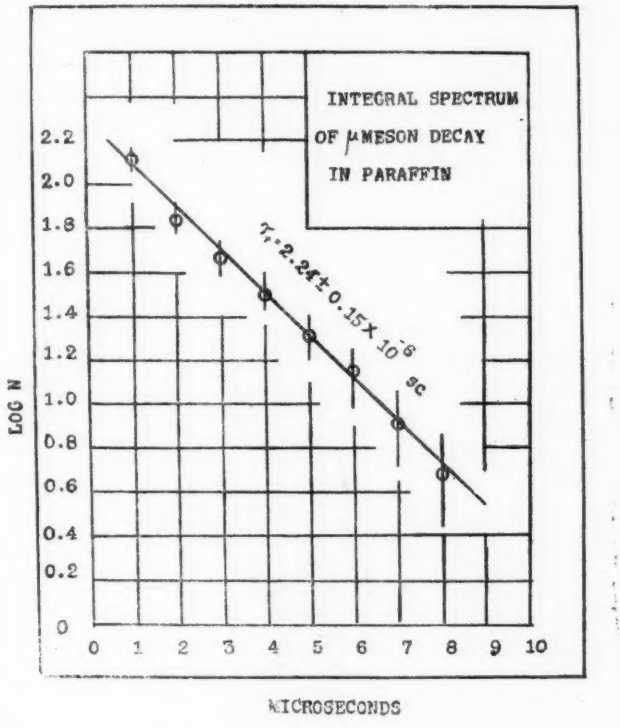


FIG. 6

fitted by the method of least squares to the observed points comes out as $2{\cdot}24 \pm 0{\cdot}15$ microseconds. The most recent value for the life-time of

positive mesons is that of Bell and Hinks (1951) and is equal to $2 \cdot 22 \pm 0 \cdot 02$ microseconds. The best earlier measurements are of Rossi and Nereson (1943) $2 \cdot 15 \pm 0 \cdot 07$ microseconds, Ticho (1948) $2 \cdot 11 \pm 0 \cdot 10$ microseconds, and Conversi and Pancini (1946) $2 \cdot 33 \pm 0 \cdot 15$ microseconds.

## ACKNOWLEDGEMENT

I wish to express my gratitude to Prof. H. J. Bhabha, F.R.S., for suggesting the problem and for helpful guidance and keen interest throughout the work. I am very much indebted to Prof. D. D. Kosambi, for suggesting the method of statistical analysis. I wish to express my grateful thanks to Mr. A. B. Sahiar for valuable discussions.

## SUMMARY

The disintegration curves of positive $\mu$-mesons at rest in two absorbers lead and paraffin have been determined experimentally by an oscilloscopic method using cosmic-ray mesons at sea level as the source of $\mu$-mesons. The mean life-time for positive mesons in lead is $2 \cdot 24 \pm 0 \cdot 17$ microseconds, and in paraffin the mean life-time is $2 \cdot 24 \pm 0 \cdot 15$ microseconds. A complete description of the equipment built for this experiment is given.

## APPENDIX

### Statistical Analysis of the Results in the Case of Lead

The following method was used to test whether the experimental points obtained are self-consistent and can be fitted into a decay curve.

The photographs were projected by means of an enlarger on a polarograph paper and the angles subtended at the centre of the circle by the arcs were measured correct to 5° (0·014 microseconds). The observations were grouped into 26 classes of 10° interval starting from 90°. If $n_0$, $n_1$, $n_2$, $n_3$, etc., are the number of events falling into the classes 0, 1, 2, 3, etc., then we define

$$N = n_0 + n_1 + n_2 + n_3 + n_4 + \ldots\ldots\ldots$$

$$m = \frac{0n_0 + 1n_1 + 2n_2 + 3n_3 + \ldots\ldots\ldots}{n_0 + n_1 + n_2 + n_3 + \ldots\ldots\ldots\ldots}$$

$$Z = \frac{m}{m+1}$$

then the expected values for the various intervals, according to the method given by Kosambi (1949) are,

$$\lambda_0 = (1 - Z)\,N$$

$$\lambda_1 = \lambda_0 Z$$

$$\lambda_2 = \lambda_1 Z$$

$$\ldots\ldots\ldots\ldots$$

$$\ldots\ldots\ldots\ldots$$

In the following table the observed and expected number for the various classes are given. In those cases where the number of events in the class were less than 10, two or more classes were grouped together such that the total was always more than 10. It is seen that for 13 degrees of freedom the total $\chi^2$ is about 15·5. $P_{13}(\chi^2 \geqslant 15{\cdot}5) = 0{\cdot}80$. Therefore $\chi^2$ is not significant.

The mean life-time $\tau$ for decay is connected with Z by the following relation

$$Z = e^{-t/\tau},$$

where $t = 0{\cdot}277$ microseconds, the time corresponding to the 10° intervals chosen. The calculated value of Z is 0·881. Therefore the mean life-time for decay is $2{\cdot}193 \times 10^{-6}$ seconds.

TABLE

| Class | | Number obtained | Number expected | $\chi^2$ |
|---|---|---|---|---|
| 0 | 90°–100° | 34 | 33·62 | .. |
| 1 | 100 –110 | 30 | 29·64 | .. |
| 2 | 110 –120 | 28 | 26·11 | .. |
| 3 | 120 –130 | 25 | 23·01 | .. |
| 4 | 130 –140 | 20 | 20–29 | .. |
| 5 | 140 –150 | 13 | 17·87 | 1 |
| 6, 7 | 150 –170 | 21 | 32·49 | 4 |
| 8, 9 | 170 –190 | 20 | 25·24 | 1 |
| 10, 11 | 190 –210 | 20 | 19·60 | .. |
| 12, 13 | 210 –230 | 14 | 15·22 | .. |
| 14, 15 | 230 –250 | 20 | 11–82 | 5 |
| 16, 17, 18 | 250 –280 | 12 | 12·97 | .. |
| 19, 20, 21 | 280 –310 | 15 | 9·06 | 4 |
| 22, 23, 24, 25, 26 | 310 –360 | 11 | 9·01 | 0·5 |
| | | | | 15·05 |

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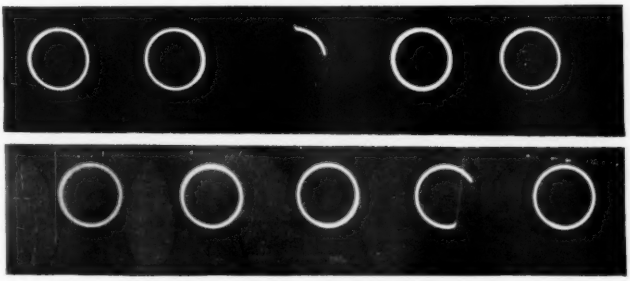

FIG. 2. Typical oscilloscopic records of the $\mu$-meson decay events registered.

# THE KJELDAHL METHOD OF NITROGEN DETERMINATION

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In the course of an investigation on the nitrogen metabolism of soil fungi started in collaboration with the University Botany Laboratory, it was found necessary to reinvestigate the condition for a correct estimate of the nitrogen content of fungal mat as well as the substrate. A critical review by Kirk[1] of the conditions clearly brought out the circumspection needed in the choice of oxidising agents. Patel and Sreenivasan[4] as well as Willits, Coe and Ogg[7] have drawn attention to the danger of nitrogen loss in the case of selenium catalysis and the latter authors recommend the use of mercuric oxide in the digestion of refractory nitrogen compounds. Miller and Houghton,[2] however, have shown that in the case of Tryptophan, quantitative yields of nitrogen required seven hours' digestion while White and Secer[6] consider that less than two hours will be adequate. Using hydrogen peroxide as the oxidiser, Miller and Miller[3] have reported a complete recovery of nitrogen in ten minutes.

The present study reports the results of a reinvestigation of the problem with reference to the major problem on hand. Fungal mats of *Fusarium vasinfectum* as well as of *Fusarium moniliforme*, the substrate on which these fungi were grown and a few pure compounds have been studied.

## Experimental

The standard procedure for microkjeldahl estimations have been used throughout. The results presented in each case is the mean of at least six estimations.

The relative amounts of nitrogenous material, digestion mixture containing the catalyst and other material used are as follows:

Nitrogenous material: 50 mg.
Concentrated sulphuric acid (nitrogen free): 2·5 ml.
Digestion mixture: 150 mg.

Where mercuric oxide was used as the catalyst for the oxidation, the alkali required for liberating the ammonia contained sodium thiosulphate (40% NaOH and 5% thiosulphate). The ammonia was recovered by steam

* Government of India Scholar.

distillation at a pH of 7·4 using a phosphate buffer in a Parnas-Wagner apparatus over a period of 4 minutes and absorbed in a 2% solution of boric acid. The ammonia was then titrated against standard centinormal hydrochloric acid using Mazuazaga indicator (a mixed indicator containing bromcresol green and methyl red).

The experimental results obtained are given in Tables I to V and Figs. 1 and 2.

TABLE I

*Composition of Digestion Mixtures*

| No. | Components used | | | Proportion of components by weight *a : b* or *a : b : c* |
|---|---|---|---|---|
| | *a* | *b* | *c* | |
| 1 | Potassium sulphate | Cupric sulphate | | 3 : 1 |
| 2 | do | Mercuric oxide | | 5 : 1 |
| 3 | do | Selenium | | 10 : 1 |
| 4 | do | Cupric sulphate | Mercuric oxide | 5 : 1 : 1 |
| 5 | do | do | Selenium | 8 : 2 : 1 |
| 6 | do | Mercuric oxide | do | 8 : 1 : 1 |
| 7 | do | Cupric sulphate | do | 5 : 1 : 1 |
| 8 | do | Mercuric Oxide | do | 5 : 1 : 1 |

TABLE II

*Recovery of Nitrogen from Ammonium Sulphate*

| Catalyst | % Recovery of nitrogen after digestion for minutes | | | | | | |
|---|---|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 30 | 45 | 60 |
| 1 | | | 100 ± 0·2 | | | | |
| 2 | | | 100 ± 0·1 | | | | |
| 3 | 100 | 98·98 | 98·0 | 96·2 | 92·0 | 90·4 | 90·4 |
| 4 | | | 100 − 0·1 | | | | |
| 5 | 100 | 100 | 99·4 | 97·2 | 94·8 | 92·0 | 90·0 |
| 6 | 100·1 | 100 | 100 | 98·4 | 94·2 | 91·4 | 90·05 |

TABLE III

*Estimation of Nitrogen in Pyridine, Methionine and Tryptophan*

| Compound | % Catalyst | Clarification time | % Nitrogen recovered after digestion for minutes | | | | |
|---|---|---|---|---|---|---|---|
| | | | 5 | 10 | 15 | 30 | 45 |
| Pyridine | 3 | 8·0 | 96·4 | 99·2 | 99·6 | 97·4 | 97·8 |
| | 5 | 8·5 | 95·4 | 99·6 | 98·9 | 98·8 | 93·4 |
| | 6 | 8·5 | 94·2 | 99·8 | 99·4 | 99·2 | 98·8 |
| Methionine | 3 | 9·5 | 94·2 | 98·4 | 99·8 | 98·4 | 94·2 |
| | 5 | 9·5 | 90·4 | 95·4 | 98·8 | 97·2 | 94·4 |
| | 6 | 9·5 | 92·4 | 95·8 | 99·4 | 98·2 | 96·4 |
| Tryptophan | 3 | 8·5 | 90·4 | 92·8 | 94·2 | 96·4 | 96·4 |
| | 5 | 8·5 | 91·2 | 94·5 | 95·6 | 95·4 | 96·2 |
| | 6 | 9·0 | 90·1 | 94·8 | 96·4 | 97·8 | 97·4 |

TABLE IV

*Estimation of Nitrogen in the Presence of Sugars*

| Amount of Nitrogen as urea in 2 ml. | Bromine water added ml. | Sucrose added mg. | Nitrogen recovered | % recovery |
|---|---|---|---|---|
| 2 mg. | 0·45 | 50 | 1·98 | 99·0 |
| 2 mg. | 0·60 | 100 | 1·982 | 99·1 |
| 2 mg. | 0·90 | 150 | 1·978 | 98·9 |

TABLE V

*Estimation of Nitrogen in Peptone*

| Catalist | Time for clarification in minutes | % Nitrogen recovered after digestion for minutes | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 5 | 10 | 15 | 20 | 30 | 45 | 60 |
| 1 | 12·0 | 12·2 | 12·8 | 13·6 | 14·0 | 14·1 | 14·1 | 14·04 |
| 2 | 10·5 | 12·5 | 13·2 | 13·6 | 14·0 | 14·1 | 14·1 | 14·05 |
| 3 | 8·5 | 11·4 | 13·6 | 14·1 | 14·0 | 13·4 | 12·8 | 12·75 |
| 4 | 11·5 | 12·0 | 13·1 | 13·9 | 14·1 | 14·0 | 14·04 | 14·1 |
| 5 | 8·5 | 12·6 | 13·8 | 14·0 | 14·0 | 14·0 | 13·6 | 13·0 |
| 6 | 9·0 | 11·8 | 13·6 | 14·0 | 14·1 | 14·0 | 14·1 | 13·94 |

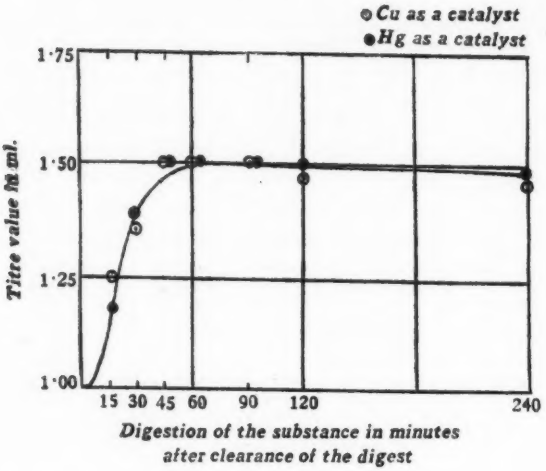
⊙ Cu as a catalyst
● Hg as a catalyst
1·75
1·50
1·25
1·00
Titre value in ml.
15 30 45 60 90 120 240
Digestion of the substance in minutes
after clearance of the digest

FIG. 1

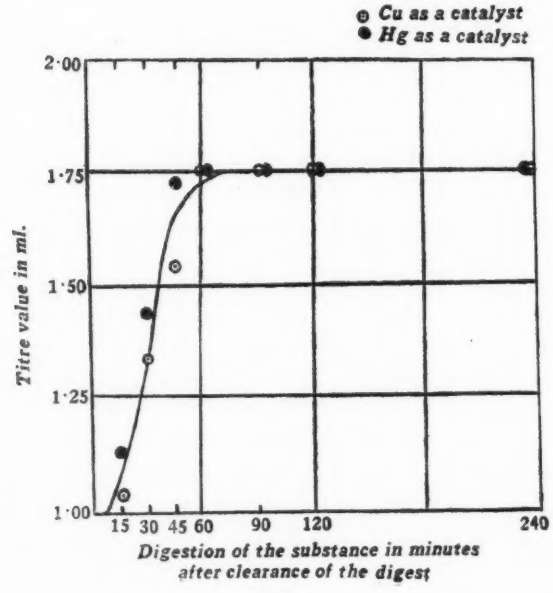
⊙ Cu as a catalyst
● Hg as a catalyst
2·00
1·75
1·50
1·25
1·00
Titre value in ml.
15 30 45 60 90 120 240
Digestion of the substance in minutes
after clearance of the digest

FIG. 2

In standardising the conditions for estimation of nitrogen in the substrate on which the fungi were grown, it was found that a modification of the method of Portener[5] using a potassium sulphate-cupric sulphate catalyst but omitting 'superoxol' was quite satisfactory. Typical observations have been recorded in Table IV.

In the case of tryptophan, conditions good enough for other nitrogenous compounds failed to give satisfactory yields of nitrogen and the variations of conditions tried are reported in Table VI.

TABLE VI

*Estimation of Nitrogen in Tryptophan Using Different Catalyst Concentrations*

In all cases the solution became clear in about 8 minutes

| Catalyst | % Nitrogen recovered after a digestion time in minutes following clarification | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 5 | 10 | 20 | 30 | 45 | 60 | 90 | 120 |
| $K_2SO_4$ : Se 10 : 1 .. | 90·4 | 91·8 | 93·4 | 96·8 | 96·8 | 97·8 | .. | .. |
| 10 : 1·5 .. | 91·2 | 92·4 | 92·8 | 94·8 | 97·2 | 97·1 | .. | .. |
| 10 : 2 .. | 91·0 | 92·8 | 93·8 | 94·8 | 98·4 | 98·6 | .. | .. |
| 10 : 3 .. | 92·1 | 92·6 | 94·2 | 95·4 | 98·4 | 97·4 | .. | .. |
| 10 : 4 .. | 90·1 | 92·8 | 95·4 | 96·8 | 94·2 | 94·6 | .. | .. |
| Cat. 7 of Table I .. | 90·4 | 91·2 | 94·8 | 96·4 | 98·2 | 98·4 | 99·1 | 99·0 |
| Cat. 8 of Table I .. | 90·4 | 92·4 | 94·8 | 96·4 | 97·8 | 98·4 | 99·2 | 99·6 |

## DISCUSSION

With nitrogenous compounds readily converted into ammonium salts, cupric and mercuric ions are found to be satisfactory catalysts. With simpler compounds, a digestion time of five minutes after clarification is found to be adequate and there is no serious loss through oxidation even after one hour. From the figures (1 and 2) it will be further noticed that even with the fungal mats, these same catalysts are efficient but clarification required about 20 minutes and for the maximum yield of nitrogen about 45 minutes more are needed. Up to four hours there does not appear to be any reduction in nitrogen recovery, so that these catalysts were chosen for the subsequent investigations.

With selenium as the catalyst for the oxidation, a digestion time beyond ten minutes was invariably accompanied by loss of nitrogen. Using refractory nitrogen compounds, however, the only satisfactory catalysts are those which include selenium as a component. Even here, the relative efficiency and accuracy vary with the heterocyclic compound or amino acid studied. Maximum recovery of nitrogen is possible with pyridine in about fifteen minutes, after which there is loss of nitrogen. The behaviour of methionine is quite similar, but tryptophan is quite resistant and a digestion time of nearly two hours is found necessary, using selenium and with cupric or mercuric ions as catalysts.

Evidence is as yet inadequate to properly account for the loss of nitrogen in the presence of selenium. It is well known that between 200 and 600° C., selenium is a good dehydrogenating agent and all the Kjeldahl estimations take place within this range of temperature as the sulphuric acid is generally kept near its boiling point. Further any hydrogen selenide that might be formed by such dehydrogenation can be oxidised by the sulphuric acid to elementary selenium. It is quite likely that when the oxidation of the organic compound is nearly complete, dehydrogenation of the ammonium ion takes place, the nitrogen being lost either as elementary nitrogen or as one of the oxides. Experiments are in progress to elucidate fully the action of selenium in this reaction. The tentative picture suggested is consistent with the observations in Table VI that a maximum recovery of 99·6% of the nitrogen is possible even in the case of tryptophan after which there is a progressive reduction of recovery.

Estimations of nitrogen in the presence of carbohydrates is often troublesome and time-consuming but using bromine water in small amounts, the estimation is found to be comparatively easy. As can be seen from Table IV, a 99% recovery of nitrogen is possible even in the case of urea which can react with bromine with the formation of nitrogen. The choice of urea as a test case was to assess the accuracy since amino compounds and even ammonium salts may react with bromine water. The results obtained show that even under such adverse circumstances the method is reasonably accurate.

Even in the case of a system containing a complex mixture of nitrogenous compounds as in peptone, the use of copper sulphate as catalyst is found most satisfactory and the results as shown in Table V confirm the observations with the pure compounds.

Schwab and Schwab-Agaldis appear to have studied the kinetics of the reaction by observing the flow-rate of the gaseous products[5a] taking aniline as the nitrogenous compound. The mechanism suggested by these authors

differs from the picture presented here and further work is obviously necessary before a proper mechanism can be established for the reaction.

The authors thank Dr. T. S. Sadasivan, F.A.SC., of the University Botany Department, for helpful discussion. One of us (K. V. S.) has to thank the Government of India for a Fellowship which enabled him to take part in these studies.

## SUMMARY

The conditions for the estimation of nitrogen by the Kjeldahl method have been studied and the limitations examined. A tentative picture of the action of selenium in the reaction is also indicated.

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# THE CHARACTERISTIC VIBRATIONS OF A RECTANGULAR LATTICE

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## A. Introduction

In a previous paper,[1] the author had shown that for a linear lattice with $p$ atoms in its unit cell, there are $(2p - 1)$ frequencies for which the group velocity of the waves traversing along the lattice vanish, and it was further proved that any arbitrary initial disturbance ultimately settles into a superposition of these $(2p - 1)$ characteristic vibrations, the amplitudes of vibrations at any instant being proportional to the square root of the time elapsed. These results, however are not peculiar to linear lattices alone and we have reason to believe that for periodic lattices in two and three dimensions,[2] there are $(8p - 2)$ and $(24p - 3)$ frequencies respectively for which the group velocity of the waves associated with them vanish, $p$ in each case representing the number of atoms in an unit cell of the lattice. It is the object of the present paper to prove the above statement and extend the results of the previous paper to the case of a rectangular lattice, which for simplicity is assumed to consist of one particle in each of its unit cells.

## 1. The Characteristic Frequencies

We shall denote the lattice distances by $d_1$ and $d_2$ and let $\tan \lambda = \frac{d_2}{d_1}$. The position of any particle is specified by means of the ordered pair of integers $(l, m)$ and the components of the displacements of the particles along the $x$ and $y$ directions are denoted by $x_{l,m}$ and $y_{l,m}$. We restrict the interaction of any particle to its immediate and diagonal neighbours only and neglect the effect of the forces caused on it by the displacements of the more distant neighbours. Since the interacting forces are assumed to be central, this assumption places a restriction on the magnitudes of $d_1$ and $d_2$ and implies that $(d_1^2 + d_2^2)^{\frac{1}{2}}$ is less than both $2d_1$ and $2d_2$. The potential energy of the lattice now becomes a function of three force constants $\alpha$, $\beta$, $\gamma$ and as $(x_{l,m} \cos \lambda + y_{l,m} \sin \lambda)$ is the resolved part of the displacement of the particle $(l, m)$ along the diagonal joining it to the particle $(l + 1, m + 1)$,

we have the following expressions for the potential and kinetic energies of the lattice.

$$2T = M \sum_{l,m} (\dot{x}_{l,m}^2 + \dot{y}^2_{l,m}) \tag{1}$$

$$2V = \alpha \sum_{l,m} (x_{l,m} - x_{l+1,m})^2 + \beta \sum_{l,m} (y_{l,m} - y_{l,m+1})^2$$
$$+ \gamma \sum_{l,m} (x_{l,m} \cos\lambda + y_{l,m} \sin\lambda - x_{l+1,m+1} \cos\lambda - y_{l+1,m+1} \sin\lambda)^2$$
$$+ \gamma \sum_{l,m} (x_{l,m} \cos\lambda - y_{l,m} \sin\lambda - x_{l-1,m+1} \cos\lambda + y_{l-1,m+1} \sin\lambda)^2,$$

the summation extending over all the particles of the lattice.

When the lattice extends indefinitely along both sides, it is necessary to assume the convergence of the series (1); this, however, would be secured in the problem which we consider since the total energy of the lattice, which is due to an initial disturbance imparted to a finite region of the lattice, is a constant.

The equations of motion of the particles are now given by

$$-M\ddot{x}_{l,m} = \alpha (2x_{l,m} - x_{l+1,m} - x_{l-1,m}) \tag{2}$$
$$+ \gamma \cos\lambda \begin{cases} 4x_{l,m} \cos\lambda - x_{l+1,m+1} \cos\lambda - y_{l+1,m+1} \sin\lambda \\ - x_{l-1,m+1} \cos\lambda + y_{l-1,m+1} \sin\lambda - x_{l+1,m-1} \cos\lambda \\ + y_{l+1,m-1} \sin\lambda - x_{l-1,m-1} \cos\lambda - y_{l-1,m-1} \sin\lambda \end{cases}$$

$$-M\ddot{y}_{l,m} = \beta (2y_{l,m} - y_{l,m+1} - y_{l,m-1}),$$
$$+ \gamma \sin\lambda \begin{cases} 4y_{l,m} \sin\lambda - x_{l+1,m+1} \cos\lambda - y_{l+1,m+1} \sin\lambda \\ + x_{l-1,m+1} \cos\lambda - y_{l-1,m+1} \sin\lambda + x_{l+1,m-1} \cos\lambda \\ - y_{l+1,m-1} \sin\lambda - x_{l-1,m-1} \cos\lambda - y_{l-1,m-1} \sin\lambda \end{cases}$$

We shall assume wave solutions for these equations of the type

$$x_{l,m} = f_1 e^{i(\omega t + l\theta_1 + m\theta_2)}$$
$$y_{l,m} = f_2 e^{i(\omega t + l\theta_1 + m\theta_2)}, \tag{3}$$

where $f_1$ and $f_2$ are functions of the two variables $\theta_1$ and $\theta_2$.

Substituting equations (3) in (2), we get

$$f_1 [f(\theta_1\theta_2) - M\omega^2] + f_2 \psi(\theta_1\theta_2) = 0$$
$$f_1 \psi(\theta_1\theta_2) + f_2 [\phi(\theta_1\theta_2) - M\omega^2] = 0, \tag{4}$$

where

$$f(\theta_1\theta_2) = 2\alpha(1 - \cos\theta_1) + 4\gamma\cos^2\lambda(1 - \cos\theta_1\cos\theta_2)$$

$$\phi(\theta_1\theta_2) = 2\beta(1 - \cos\theta_2) + 4\gamma\sin^2\lambda(1 - \cos\theta_1\cos\theta_3) \quad (5)$$

and $\psi(\theta_1\theta_2) = 4\gamma\sin\lambda\cos\lambda\sin\theta_1\sin\theta_2$.

Eliminating $f_1$ and $f_2$ from equations (4) we get

$$M^2\omega^4 - M\omega^2[f(\theta_1\theta_2) + \phi(\theta_1\theta_2)] + f(\theta_1\theta_2)\phi(\theta_1\theta_2) - \psi^2(\theta_1\theta_2) = 0 \quad (6)$$

Since from (6), $\omega$ is a periodic function of $\theta_1$ and $\theta_2$, we shall consider only the values of $\theta_1$ and $\theta_2$ lying inside the intervals $0 \leqslant \theta_1 \leqslant 2\pi$; and $0 \leqslant \theta_2 \leqslant 2\pi$. Also, by a comparison of (3) with the usual form of the wave function, we get $k = \frac{1}{\lambda} = \frac{1}{2\pi}\sqrt{\frac{\theta_1^2}{d_1^2} + \frac{\theta_2^2}{d_2^2}}$, where $\lambda$ is the wavelength of a wave. More than the individual waves, greater importance attaches to the groups of waves and their velocities since it is only these physical entities that are accessible to any observation and measurement. The group velocity of the waves defined by $\frac{d\nu}{dk}$ will vanish when both $\frac{\partial\omega}{\partial\theta_1}$ and $\frac{\partial\omega}{\partial\theta_2}$ are equal to zero.

We have now from (6)

$$A\frac{\partial\omega}{\partial\theta_1} = K_1\sin\theta_1, \quad (7a)$$

where

$$A = M\omega[2M\omega^2 - f(\theta_1\theta_2) - \phi(\theta_1\theta_2)]$$

$$K_1 = \alpha[M\omega^2 - \phi(\theta_1\theta_2)] + 2\gamma\cos\theta_2[M\omega^2 - f(\theta_1\theta_2)\sin^2\lambda - \phi(\theta_1\theta_2)\cos^2\lambda] + 16\gamma^2\sin^2\lambda\cos^2\lambda\sin^2\theta_2\cos\theta_1 \quad (8)$$

and $$A\frac{\partial\omega}{\partial\theta_2} = K_2\sin\theta_2. \quad (7b)$$

where $K_2$ is defined in a similar manner as (8).

It can therefore easily be seen that both $\frac{\partial\omega}{\partial\theta_1}$ and $\frac{\partial\omega}{\partial\theta_2}$ vanish for the set of points (0, 0); (0, $\pi$); ($\pi$, 0) and ($\pi$, $\pi$). Excluding the point (0, 0) which corresponds to a translation of the entire lattice, we have for the frequencies associated with the remaining three points the following expressions:

$$
\begin{aligned}
&(1)\quad M u_1^2 = f(0, \pi) = 8\gamma \cos^2 \lambda \\
&\qquad M u_2^2 = \phi(0, \pi) = 4(\beta + 2\gamma \sin^2 \lambda) \\
&(2)\quad M v_1^2 = f(\pi, 0) = 4(\alpha + 2\gamma \cos^2 \lambda) \\
&\qquad M v_2^2 = \phi(\pi, 0) = 8\gamma \sin^2 \lambda \\
&(3)\quad M w_1^2 = f(\pi, \pi) = 4\alpha \text{ and} \\
&\qquad M w_2^2 = \phi(\pi, \pi) = 4\beta. \qquad (9)
\end{aligned}
$$

It follows now from (7) that the group velocity of the waves associated with each of these six characteristic frequencies is equal to zero.

The case of a square lattice is particularly simple and interesting. Here we have $\alpha = \beta$ and $\lambda = \frac{\pi}{4}$ and only three of the six frequencies given above are distinct.

## 2. The Effect of an Initial Disturbance

We shall suppose that initially the particle at the origin receives a small displacement whose components parallel to the axes are $a$ and $b$ respectively and that all other particles are at rest.

$$
\begin{aligned}
&(i.e.)\quad x_{l,m}(0) = a\delta_{l0}\delta_{m0} \qquad (10)\\
&\qquad y_{l,m}(0) = b\delta_{l0}\,\delta_{m0} \text{ and } \dot{x}_{l,m}(0) = \dot{y}_{l,m}(0) = 0
\end{aligned}
$$

for all $l$ and $m$. If the values of $f_r$ $(r = 1, 2)$ corresponding to the frequencies $\pm\omega_s$ $(s = 1, 2)$ are denoted by $f_{r,s}$ and $f_{r,2+s}$, following Nagendra Nath,[3] we obtain the general expressions for the displacements of the particles at any time by superposing wave solutions of the type (3) for all values of $\theta_1$ and $\theta_2$ lying in the interval $(0, 2\pi)$. We get

$$
\begin{aligned}
x_{l,m} = {} & \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} (f_{11}\, e^{i\omega_1 t} + f_{13} e^{-i\omega_1 t}) \text{ exp. } i(l\theta_1 + m\theta_2)\, d\theta_1 d\theta_2 \\
& + \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} (f_{12}\, e^{i\omega_2 t} + f_{14} e^{-i\omega_2 t}) \text{ exp. } i(l\theta_1 + m\theta_2)\, d\theta_1 d\theta_2 \qquad (11)
\end{aligned}
$$

$$
\begin{aligned}
y_{l,m} = {} & \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} (f_{21}\, e^{i\omega_1 t} + f_{23}\, e^{-i\omega_1 t}) \text{ exp. } i(l\theta_1 + m\theta_2)\, d\theta_1 d\theta_2 \\
& + \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} (f_{22}\, e^{i\omega_2 t} + f_{24} e^{-i\omega_2 t}) \text{ exp. } i(l\theta_1 + m\theta_2)\, d\theta_1 d\theta_2 \qquad (12)
\end{aligned}
$$

With the help of equations (4) and the initial conditions (10), we can express the values of $f_{rs}$ as functions of $\theta_1$ and $\theta_2$. We have from (11)

$$x_{l,m}(0) = \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi}(f_{11}+f_{12}+f_{13}+f_{14})\exp.\, i(l\theta_1+m\theta_2)\,d\theta_1\,d\theta_2$$

$$\dot{x}_{l,m}(0) = \frac{i}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi}\{\omega_1(f_{11}-f_{13})+\omega_2(f_{12}-f_{14})\}\exp.\, i(l\theta_1+m\theta_2)\,d\theta_1 d\theta_2$$

By expanding $\sum_{r=1}^{4} f_{1r}$ as a Fourier series in $\theta_1$ and $\theta_2$ in the form

$$\sum_{r=1}^{4} f_{1r} = \sum_{+\infty}^{-\infty}\sum_{+\infty}^{-\infty} \mathbf{A}_{jk}\, e^{i(j\theta_1+k\theta_2)} \tag{14}$$

we get on substituting (14) in (13)

$$x_{l,m}(0) = \frac{1}{8\pi^2}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\mathbf{A}_{jk}\,\mathbf{I}_{jl}\,\mathbf{I}_{km}$$

$$= \tfrac{1}{2}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\mathbf{A}_{jk}\,\delta_{-jl}\,\delta_{-km}$$

$$= \tfrac{1}{2}\,\mathbf{A}_{-l-m}, \text{ where we write}$$

$$\mathbf{I}_{lm} = \int_0^{2\pi} e^{i(l+m)\theta}d\theta$$

Hence we get $\sum_{r=1}^{4} f_{1r} = 2a$ (15)

Similarly we have $\sum_{r=1}^{4} f_{2r} = 2b$ (16)

and $\sum_{r=1,2}\omega_r(f_{1r}-f_{1,2+r}) = \sum_{r=1,2}\omega_r(f_{2r}-f_{2,2+r}) = 0$ (17)

Now we get from (4), $f_{2r}\,\psi(\theta_1\theta_2) = f_{1r}\,[\mathrm{M}\omega_r^2 - f(\theta_1\theta_2)]$ and hence from (16) and (17) we have

$$\sum_{r=1,2}\omega_r^2(f_{1,r}+f_{1,2+r}) = 2\,\frac{(\psi b + fa)}{\mathrm{M}} \tag{18}$$

and

$$\sum_{r=1,2}\omega_r^3(f_{1r}-f_{1,2+r}) = 0 \tag{19}$$

Solving these equations we get,

$$f_{11} = f_{13} = \frac{a(M\omega_2^2 - f) - \psi b}{M(\omega_2^2 - \omega_1^2)} \qquad (20)$$

$$f_{12} = f_{14} = \frac{a(M\omega_1^2 - f) - \psi b}{M(\omega_1^2 - \omega_2^2)}$$

and two similar expressions for $f_{21}$ and $f_{22}$.

With these values for $f_{11}$ and $f_{12}$, equation (17) can now be rewritten as

$$x_{l,m} = \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} f_{11}\,(e^{i\omega_1 t} + e^{-i\omega_1 t})\, e^{i(l\theta_1 + m\theta_2)}\, d\theta_1\, d\theta_2 \qquad (21)$$

$$+ \frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{2\pi} f_{12}\,(e^{i\omega_2 t} + e^{-i\omega_2 t})\, e^{i(l\theta_1 + m\theta_2)}\, d\theta_1 d\theta_2$$

The asymptotic value of the above integral for large values of $t$ can be obtained by means of an extension of Kelvin's method of stationary phases for double integrals. We shall consider the integral

$$I = \int_\Delta f(x, y)\ \text{exp.}\ i\,[\omega(x, y)\, t + lx + my]\, dx\, dy, \qquad (A)$$

where $f(x, y)$ is integrable in $\Delta$ and $t$ is large compared to $l$ and $m$ (*i.e.*) $t = 0(l^2 + m^2)$. We shall assume that the region of integration contains only one stationary point of $\omega(x, y)$ at $(x_0 y_0)$. When the region of integration contains several stationary points of $\omega(x, y)$, it can be split up into subregions such that $\omega(x, y)$ has only one stationary point in each of these subregions. Since the exponent in the integrand is a very rapidly fluctuating function when $t$ is large, the most important contribution to the integral arises only from a region in the neighbourhood of $(x_0 y_0)$ at which $\omega(x, y)$ is stationary. We have, if $x - x_0 = \xi$ and $y - y_0 = \eta$, for small values of $\xi$ and $\eta$,

$\omega(x, y) = \omega(x_0 y_0) + \frac{1}{2}(a\xi^2 + 2h\xi\eta + b\eta^2)$, where $a$, $h$, $b$ are the values of $\frac{\partial^2\omega}{\partial x^2}, \frac{\partial^2\omega}{\partial x \partial y}, \frac{\partial^2\omega}{\partial y^2}$ at the point $(x_0 y_0)$. Hence (A) can be written as

$$I \sim f(x_0 y_0)\ \text{exp.}\ i\,[\omega(x_0 y_0)\, t + lx_0 + my_0] \int_{-\xi_0}^{+\xi_0}\int_{-\eta_0}^{+\eta_0} e^{\frac{it}{2}(a\xi^2 + 2h\xi\eta + b\eta^2)}\, d\xi d\eta \qquad (22)$$

We transform the variables $\xi$, $\eta$ to a new set of variables $\sigma$ and $\rho$ given by

$$ta\left(\xi + \frac{h}{a}\eta\right)^2 = \sigma^2$$

$$\frac{(ab - h^2)}{a} t\eta^2 = \rho^2;$$

the limits for $\sigma$ and $\rho$ can be taken to be $\pm \infty$ without any appreciable error. Hence if $ab > h^2$, and $a > 0$ (22) becomes

$$I \sim \frac{f(x_0y_0)}{t(ab - h^2)^{\frac{1}{2}}} \exp.\, i\,[\omega(x_0y_0)\,t + lx_0 + my_0] \int_{-\infty}^{+\infty} e^{-\sigma^2/2i}\, d\sigma \int_{-\infty}^{+\infty} e^{-\rho^2/2i}\, d\rho$$

$$= \frac{2\pi f(x_0y_0)}{t(ab - h^2)^{\frac{1}{2}}} \exp.\, i\,[\omega(x_0y_0)\,t + lx_0 + my_0 + \pi/2)$$

If $(ab - h^2)$ is negative, then we have

$$I \sim \frac{2\pi f(x_0y_0)}{t(h^2 - ab)^{\frac{1}{2}}} \exp.\, i\,[\omega(x_0y_0)\,t + lx_0 + my_0]. \tag{23}$$

In a similar way, the value of the integral $I_1 = \int_\Delta f(x, y) \exp.\, i\,[-\omega(x, y)t + lx + my]\, dx\, dy$ for large values of $t$ is given by

$$I = \frac{2\pi f(x_0y_0)}{t\,|ab - h^2|^{\frac{1}{2}}} \exp.\, i\left[-\omega(x_0y_0)\,t + lx_0 + my_0 - \epsilon_{ab}\frac{\pi}{2}\right] \tag{24}$$

where $\epsilon_{ab}$ takes the values 1 or 0 according as $ab \gtrless h^2$.

Turning to the integral (21) we note that when $\theta_1$ and $\theta_2$ take any of the values

$$(0, \pi);\ (\pi, 0) \text{ and } (\pi, \pi), \text{ we have}$$

$$f_{11}(\theta_1\theta_2) = a;\ f_{22}(\theta_1\theta_2) = b$$

$$f_{12}(\theta_1\theta_2) = f_{21}(\theta_1\theta_2) = 0.$$

Also at these points,

$$2M\omega_1 \frac{\partial^2\omega_1}{\partial\theta_r^2} = \frac{\partial^2 f}{\partial\theta_r^2};\ 2M\omega_2 \frac{\partial^2\omega_2}{\partial\theta_r^2} = \frac{\partial^2\phi}{\partial\theta_r^2}\ (r = 1, 2)$$

and $$\frac{\partial^2\omega_r}{\partial\theta_1\partial\theta_2} = 0.$$

Hence if $w_1 > u_1$, and $w_2 > v_2$, applying the results (23) and (24) to the integral (21) we get

$$x_{l,m} = \frac{2a}{\pi t}\left[\frac{(-1)^m \cos u_1 t}{(w_1^2 - u_1^2)^{\frac{1}{2}}} + \frac{(-1)^{l+1} \sin v_1 t}{u_1} + \frac{(-1)^{l+m} w_1 \cos w_1 t}{u_1 (w_1^2 - u_1^2)^{\frac{1}{2}}}\right. \tag{I}$$

Similarly,

$$y_{l,m}=\frac{2b}{\pi t}\left[\frac{(-1)^{m+1}\sin u_2 t}{v_2}+\frac{(-1)^l\cos v_2 t}{(w_2^2-v_2^2)^{\frac{1}{2}}}+\frac{(-1)^{l+m}w_2\cos w_2 t}{v_2(w_2^2-v_2^2)^{\frac{1}{2}}}\right]$$

Two similar expressions can be derived if the initial conditions are slightly modified. If we have initially $x_{l,m}(0)=y_{l,m}(0)=0$ and $\dot{x}_{l,m}(0)=u\delta_{l0}\delta_{m0}$ ; $\dot{y}_{l,m}(0)=v\delta_{l0}\delta_{m0}$ for all $l$ and $m$, we get by an exactly similar procedure the following expressions for the displacements of the particles from their equilibrium positions.

$$x_{l,m}=\frac{2u}{\pi t}\left[\frac{(-1)^m\sin u_1 t}{u_1(w_1^2-u_1^2)^{\frac{1}{2}}}+\frac{(-1)^l\cos v_1 t}{u_1 v_1}+\frac{(-1)^{l+m}\sin w_1 t}{u_1(w_1^2-u_1^2)^{\frac{1}{2}}}\right] \qquad \text{(II)}$$

$$y_{l,m}=\frac{2v}{\pi t}\left[\frac{(-1)^m\cos u_2 t}{u_2 v_2}+\frac{(-1)^l\sin v_2 t}{v_2(w_2^2-v_2^2)^{\frac{1}{2}}}+\frac{(-1)^{l+m}\sin w_2 t}{v_2(w_2^2-v_2^2)^{\frac{1}{2}}}\right]$$

When initially, a displacement combined with a small velocity is imparted to the particle at the origin, then the components of the displacements along the $x$- and $y$-directions are given by the sum of the $x$ and $y$ components of the displacements in (I) and (II); this result follows from the principle of superposition.

## 3. Physical Interpretations

The expressions (I) and (II) clearly indicate that the movements of the particles tend asymptotically to a superposition of the six characteristic vibrations of the lattice, with a slowly diminishing amplitude which varies inversely as the time elapsed. It is interesting to note that the $x$-components of the displacements of the particles depend only on three of these modes which may be pictured as the movements of, (1) the $y$-lines moving normally against each other, (2) the $x$-lines moving tangentially in opposite directions, and (3) as the oscillations of the diagonal lines against each other along the $x$-axis. Similarly, the $y$-components of the displacements of the particles depend on three different modes of vibrations which are the tangential oscillation of the $y$-lines, the normal oscillation of the $x$-lines against each other and the movements of the diagonal lines along the $y$-axis, the frequencies of vibrations of both the diagonal lines being the same.

The decay of the vibrations according to the law $t^{-1}$ can be understood physically also. Since the initial disturbance is progressively transmitted to all the atoms around the origin, the amplitudes of the particles in the region where their movements are represented by (I) should vary approximately as the inverse square root of the area of this region and hence are inversely proportional to the time elapsed from the instant of the initial disturbance.

All these results were arrived at under the assumption that the lattice is unbounded. If however, we confine our observations to a time-interval which is large compared to the individual periods of the eigen-vibrations, but still small in comparison with the time taken by the fastest wave to reach the boundary, the above restriction can be removed and the results of the preceding sections can be seen to hold good for a finite lattice also, provided its dimensions are very large compared to that of its unit cells.

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## SUMMARY

For a rectangular lattice with one particle in each unit cell, it is shown that the group velocity of the waves vanishes for the six characteristic frequencies and that the state of movements of the particles arising out of an initial disturbance tends to a superposition of these six characteristic vibrations of the lattice. These six frequencies would reduce to three for a square lattice on account of its symmetry; in all these two cases however, the amplitudes of vibrations of the particles vary inversely as the time elapsed from the instant of the initial disturbance. The physical interpretation of these results and their applicability to the case of a finite lattice are discussed.

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